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A SYSTEMATIC STUDY OF THE ACTION OF DEFINITELY RELATED CHEMICAL COMPOUNDS UPON ANIMALS.

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(Continued from p. 152.)

Ortho-toluidine, when injected into the posterior lymph-sac of a frog, so that .017 gram of drug is present for each gram of frog, causes loss of reflexes and respiration, which comes on at once, and the animal lies wherever he is placed. The muscles and nerves respond to stimuli, but their irritability is decreased, and it is noted that reflexes are more depressed in the hind than in the fore feet. After this the reflexes improve and become almost excessive. The heart is at this time very weak, and stops shortly within an hour of the dose, in wide diastole. The reflexes are still present, but lessened for the second time. The muscles and nerves respond feebly for many minutes after death. Doses amounting to 0.001 gram have a similar effect.

If a single drop be applied to the exposed spinal cord of the frog, paraplegia at once comes on, motion being preserved in the fore legs. That the failure of motion and sensation which we have noted is dependent upon some action on the spinal cord is proved by the fact that the direct application of the drug, in the amount of one pure drop, to the exposed sciatic nerve caused very slight, if any, failure in functional activity, although extra precaution was taken that none of it should be taken by the circulation elsewhere. The loss of reflexes which at first is present we believe to be due to depression of the spinal cord, and the increase in reflex activity which later occurs to be due to some action which our present physiological knowledge does not allow us to explain, or to the disordered circulation by means of which the spinal cord is starved, so that at first its irritability is increased but finally abolished.

When applied directly to the heart of the frog in the amount of one drop, it arrests this viscus in diastole in a few minutes.

Upon the dog our results have been in accord with those in the frog. If ortho-toluidine be injected into the jugular vein, in the amount of 0.12 gram to the kilo, there is some slight change for a few moments in the rhythm of respiration, followed by quietude. Sensation is intact and so is motion. The rectal temperature is depressed 1.5° F., then speedily returns to the normal. One hour after the dose the animal seems perfectly well. No staggering occurs.

If given in so large a dose that 0.208 gram to the kilo is injected in 20 cc. water into the jugular vein, the animal instantly becomes passive and lies absolutely quiet, except that respiration is hurried. The tongue is dark blue, cyanotic and lead-colored. The pupils dilate. When put on the floor the dog cannot walk at first, but in one or two minutes can stagger about the room, the hind legs being most affected. Five minutes after the injection he can walk moderately well, but in 25 minutes after the dose he again becomes weak, staggers badly and leans against the wall for support, and falls when support is lost. The tongue, nose and mouth are now extraordinarily pale or livid. The rectal temperature is noted as having fallen 1.5° F. since the dose, and absolute muscular relaxation comes on. The respirations are slow and shallow, but expiration is forcible and quick. Consciousness is absolutely intact. The animal wags his tail feebly when spoken to. Grunting and groaning now come on with each breath, and the symptoms become more severe. The rectal temperature is now found to have fallen 1° F. more. Later forcible vomiting comes on, consisting of water and the contents of the stomach. The eyes become glazed and death seems close at hand. The temperature is now 99° F., having been normally 104° F. The respiration ceases suddenly, and at the same moment a large amount of bloody liquid, resembling methæmoglobin in color, is ejected from the stomach. The heart ceases beating three minutes later. These results correspond to those seen in the frog in respect to the return of motion after its primary loss, and the fact that respiration ceased before the heart. The loss of reflex motion and the general muscular relaxation are also identical. The peculiar bloody watery liquid ejected was probably due to a leakage of broken down blood from the mucous membrane of the stomach, owing to the great blood-changes produced by the drug, as no ruptured blood-vessels could be found.

It is worthy of remark that ortho-toluidine lowers the bodily temperature in large amounts, as do all the other members of the aniline group.

When injected in the dose of 0.05 gram to the kilo, into the jugular vein of a dog which is attached to a manometer, ortho-toluidine, in the course of about one minute and a half, causes a slight fall of pressure, accompanied by no marked change in pulse-rate, and the pressure speedily returns to the normal or even a little above it. Fifteen minutes later 0.1 gram to the kilo in 20 cc. water was injected in 20 seconds, the result being that the pressure fell very markedly, and the pulse-rate was also decreased nearly one-half. The latter, however, speedily returned to the normal, as did also the arterial pressure some seconds later. One decigram more to the kilo at this time, 16 minutes after the first dose, caused death by respiratory failure, the heart continuing to beat till some minutes later. The slowing of the pulse-rate is due to direct cardiac depression, and not vagal irritation, as is proved by the fact that severing these nerves does not cause the proper increase in rate. In other animals death took place two minutes after the injection of 0.3 gram to the kilo, preceded by a gradual fall of pulse rate and pressure, which vagal section did not relieve. As these results were reached in curarised and non-curarised animals, it would seem that they must be correct.

Meta-toluidine.

When meta-toluidine is given to a full-grown dog by the jugular vein in the dose of 0.125 gram to the kilo, death at once occurs from cardiac and respiratory failure, both functions ceasing at once. If any difference as to time occurs, respiration ceases first. When the dose by the jugular vein is 0.010 gram to the kilo, the changes produced in pulse rate, force and arterial pressure are almost nil.

If the dose be as large as 0.06 gram to the kilo, there is very marked fall of blood-pressure, followed, after a period of 30 seconds to a minute, by a rise which soon returns the arterial pressure to the normal. There is always a considerable fall of temperature in small doses. Meta-toluidine given to a dog by the jugular vein in the dose of 0.1 gram to the kilo, when free to run about, and to which no ether has been given, produces at first the greatest weakness and relaxation, so that the animal seems about to die. This rapidly passes off, so that he can soon walk in a slouchy way around the rooms and lies in a corner whenever he is allowed to do so. In the dose of 0.05 gram to the kilo virtually no change occurs so far as symptoms are concerned, save a little drowsiness. The blood always contains methæmoglobin, and is much darkened and grumous. In the frog there ensues rapidly, after a dose of 0.0015 gram to the gram into the post. lymph-sac, relaxation with arrest of all respiration, only the throat moving a little. The limbs become cyanotic, and the batrachian will soon lie on his back when so placed. Marked inco-ordination of leg movements occurs, but there seems to be no loss of motor power. Sensation is completely lost to all forms of irritation, save severe burning, and this soon passes off. Voluntary movement is preserved partially. The motor nerves are depressed, but react to stimuli. If the artery going to one limb be ligated and the poison given above, it will be found that both legs fail equally, proving that the action must be on the spinal cord, or, at any rate, not on the motor nerves. The meta-toluidine employed was prepared in the laboratory of Prof. Ira Remsen, to whom our grateful acknowledgments are due.

Para-toluidine.[1]

If this compound be given to a dog by the stomach in the dose of 0.13 gram to the kilo, all the symptoms of aniline poisoning gradually appear. If the same dose be injected *exceedingly slowly* into the jugular vein of an animal, struggles which are mild, but lacking in force, come on before the entire quantity has passed out of the syringe. When laid upon the floor and left free to run about, inability to stand, particularly in the hind legs, comes on, but eventually, in the course of about two minutes, sufficient power is gained to enable the animal to walk about in a staggering manner. The respirations are more rapid than normal, and the expiratory portion of the respiratory cycle is forcibly performed, so as to be almost sneezing in character. The pupils are much dilated. Half an hour after the dose the animal seems almost well, except for the expiratory movements which continue, and which finally accompany, an hour later, great lassitude and desire to remain quiet. From now on the dog becomes slowly but progressively worse, and is evidently more ill than before, dying at the expiration of two hours from the injection of the drug.

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[1] **It is proper to state that as para-toluidine is very insoluble, Dr. Marshall kindly prepared para-toluidine hydrochloride, a substance which is comparatively easily dissolved and administered.**

No change takes place in the bodily temperature during the first three hours, but as the symptoms of paralysis deepen, the temperature finally reaches a point several degrees below normal. Unconsciousness comes on and death takes place, the animal being utterly unconscious to all its surroundings. The blood is found to be dark-colored, abnormally fluid, and methæmoglobin is present in large amount. If the dose be as much as 0.3 gram to the kilo, the animal passes much more rapidly through the same train of symptoms as those just given, but they are also much more emphasised.

The primary struggles which come on during the injection of the drug are due to cardiac depression and the resulting nervous disturbance, as they do not occur if the dose be given with great slowness, nor when the drug is given by the stomach; and we are confirmed in this belief by our manometrical tracings, which show that such a cardiac influence is present. The other symptoms are solely due to the disorganised blood.

When from 0.02 to 0.05 gram of para-toluidine hydrochloride is injected into the body of a frog weighing 36 grams, the reflexes are rapidly lost, and the batrachian will lie for some minutes on his back when so placed by the experimenter. The fore feet and hind legs rapidly become blue and cyanosed, and, while the reflexes are still present, they are exceedingly feeble and carried out in an inco-ordinated and jerky manner.

As these changes occur in the bloodless as well as in the ordinary frog, they are at least in part due to an action on the spinal cord. That the nerves and muscles are eventually depressed we have proved again and again, but we believe this depression to be due to the altered blood, as we did not find it in the exsanguined animal.

If the heart be exposed it is seen to be beating regularly, but the blood is darker than normal. Very frequently, nearly an hour after the dose, the reflexes return to a point equal to their normal condition or above it, but are always inco-ordinated. Finally the animal lies perfectly quiet, the heart beats much more slowly, and at this time the very curious observation is made that the auricle beats twice as frequently as does the ventricle; the latter also stops before the former. The same result is reached if a single scale of the compound be placed directly on the heart-muscle of a frog whose anterior chest-wall is cut away to expose the viscus. The result under these circumstances is indeed more marked. Preceding the double beating of the auricle there is a period during which that portion of the heart seems over-distended with blood. The heart is always slowed, before these curious changes take place, by nearly one-half.

Para-toluidine, when given by the jugular vein to a dog in the proportion of 0.10 gram to the kilo, causes death of respiratory failure in 30 seconds, the heart continuing to beat for some minutes later. *Pari passu* with the arrest of respiration there is a very positive fall of pressure, eventually reaching the abscissa line. The heart-beats are not weakened till death is very near at hand, and show evidence of asphyxia, while the slowing was proved to be independent of vagal stimulation by its occurrence on section of these nerves. That the vaso-motor system is also depressed is certain, for though, as we have just related, the heart is moderately strong, a fall in blood-pressure occurs notwithstanding the asphyxia which is brought on by the arrest of respiration. Exactly the same signs follow the injection of 0.08 gram to the kilo.

When injected into the jugular vein in the proportion of 0.031 gram to the kilo, no change in arterial pressure occurs, but in the course of a few minutes the pulse-rate becomes much increased. Stimulation of the vagi at this time causes the normal amount of slowing of the heart, showing that the increased rate cannot be due to vagal depression.

SUMMARY.

Ortho-toluidine, both in the frog and dog, causes great changes in the blood and has comparatively little effect upon the heart, unless it comes directly in contact with this viscus in large amount or concentrated form. In both animals it produces a stage of decreased reflex activity and power, followed by a decrease in both these functions, which deepens into paralysis, coma and death.

The main dominant action of the compound is the breaking down of the blood, but that the entire train of symptoms do not depend on this change is shown by the fact that the drug depresses the spinal cord in the bloodless frog. In the warm-blooded animal it causes a marked fall of temperature equal to 4 or 5 degrees. Death is produced by failure of respiration. The heart eventually stops in diastole.

On the circulatory system this substance slows the pulse by depression of the heart-muscle, and does not stimulate the pneumogastric nerves. It also depresses the vaso-motor system.

On the dog and frog meta-toluidine changes the blood into methæmoglobin and produces a loss of reflex activity, dependent upon depression of the spinal cord. It lowers bodily temperature very remarkably, and exercises very little effect on the circulation unless given in exceedingly large doses. It kills chiefly by failure of respiration, unless sent *en maſse* into the heart, when it kills by cardiac and respiratory failure of a simultaneous action.

In the frog and dog the results reached with para-toluidine are identical with those of the ortho and meta compounds in the primary depression, secondary increase and final loss of reflex activity and power, so that in this respect para-toluidine and ortho-toluidine are very closely allied. The dominant action is also the destruction of the blood corpuscles and the development of methæmoglobin. It also depresses the spinal cord and kills by failure of respiration, the heart beating for some moments afterwards. The most extraordinary fact noted in regard to the compound is the double beat of the auricle to the single beat of the ventricle in the frog's heart. If brought in direct contact with the heart of the frog or mammal in large amount, it arrests this viscus in diastole. Small doses, 0.031 gram to the kilo, increase the pulse-rate, which stimulation of the vagi instantly controls. The fatal dose of ortho-toluidine by the jugular vein is 0.208 gram to the kilo; of meta-toluidine, 0.125 gram; of para-toluidine, 0.10 gram to the kilo. It is worthy of note that the lethal doses of these compounds depend upon the rapidity of injection to a very great extent. The ortho-toluidine and para-toluidine came from the establishment of Kahlbaum in Berlin.

Pyrocatechin.

Pyrocatechin, the ortho member of the group about to be considered, seems, unlike most of the compounds already studied, to be more powerful by far than the meta compound, and even more active than the para compound, hydroquinone. The injection of small quantities of pyrocatechin into the jugular vein, such as 0.0166 gram to the kilo, of the dog, produces at once epileptiform convulsions and all the evidences of poisoning by this class of compounds. The blood rapidly becomes blackish. The periods of spasms are long-continued and exceedingly severe, and death seems to occur from exhaustion and respiratory failure when the dose has been as large as 0.04 gram to the kilo. When the dose is by the stomach, a much larger amount is required. The same train of symptoms ensue under these circumstances as occur when the drug is given by the jugular vein. When given by the jugular vein, in the dose of 0.0166 gram to the kilo of dog's weight, the animal being attached to the manometer, pyrocatechin causes, along with the muscular twitchings and convulsions, a marked slowing of the pulse, the arterial pressure remaining little changed. If the dose be as large as 0.0384 gram to the kilo, the pulse is also slowed, and during the convulsion the arterial pressure is somewhat raised. Finally, however, the pulse remaining at its point of primary change, the arterial pressure sinks lower and lower, and the animal dies of respiratory failure, the respiration ceasing before the heart, which beats for some moments later. If the dose be as large as 0.075 gram to the kilo, the pulse at once becomes slower by many beats, the arterial pressure remaining almost unchanged. That this slowing of the pulse, seen also after smaller doses, is not due to the convulsions, but to vagal stimulation, is proved by the fact that it occurs in the curarised dog, and also by the all-important fact that section of these nerves at once causes as rapid a pulse-rate as in the undrugged animal under such an operation. The pulse-waves during this time are very full and strong, and the heart-beat is forcible.

The results of Brieger's studies, which are entirely confirmed by our own, may be seen in the summing up of the action of these drugs under hydroquinone.

Resorcin.

The employment of resorcin in therapeutics, both for internal and external medication, increases the interest attached to its study very considerably, and we find that other investigators have already made considerable progress in finding out its true physiological action. None of the researches which we have been able to find give, however, the relations of the drug as a meta compound, although physiologists have in two instances studied the ortho and para compounds, pyrocatechin and hydroquinone, at the same time. These investigations we shall refer to later, mentioning them after detailing our results, because the papers were read after our own studies were made, but of course acknowledging their priority.

Resorcin when injected into the jugular vein of a dog attached to a manometer, in the dose of 0.0143 gram to the kilo, produces a slight fall of arterial pressure, and slowing of the pulse to a slight extent. If the dose be as large as 0.1666 gram to the kilo of the animal's weight, this fall of pressure becomes still more marked, as does also the slowing of the pulse. That this fall of the arterial pressure is dependent on an action upon the vaso-motor system seems proved by the fact that the heart-beats give no evidence of cardiac depression, and asphyxia does not produce as great a rise of pressure as it should do. The slow pulse noted may be due to several causes, the convulsions, with the violent breathing and resulting heart-strain, the action of the drug on the heart itself or on the vagus nerve That the convulsive breathing is partly responsible for this seems proved by the fact that the same degree of slowing does not occur in the curarised animal, although it occurs to a decided extent nevertheless. That the heart is not depressed seems equally clear by reason of the strong pulse beats, and finally the vagus nerve is stimulated, since vagal section at this time allows the heart to double its number of beats, although they do not approach those of the normal dog whose vagi are cut, pointing to stimulation of their peripheral filaments. If the dose of 0.4 gram to the kilo is used there is a great fall of blood pressure, amounting to from 30 to 140 mm. of mercury, accompanied by very marked slowing of the pulse, due to the vagal stimulation.

The convulsions produced are exceedingly severe. When injected in the dose of 0.1 to 0.4 gram to the kilo, into the jugular vein in the dog free to run about, the symptoms consist in violent epileptiform convulsions, in which the animal is thrown about hither and thither and utterly unable to stand. The lethal dose by the jugular vein is about 0.7 to 1 gram to the kilo. Death is due to respiratory failure, probably from the action of the blood. These studies confirm those of Brieger[1] and Beyer.[2]

In the frog, Brieger noted that the dose of 0.005 gram of resorcin to 55 grams of frog produced convulsions followed by recovery; that 0.01 gram to a larger frog caused similar convulsions and death in six hours; very much smaller doses produced mild convulsions, and still smaller ones no convulsions at all. In the rabbit, Brieger found the dose of 0.33 gram to the kilo, by the mouth, caused convulsions for two hours, but the animal recovered in a day.

In the studies made by Beyer upon the isolated heart of the frog and terrapin, he found that solutions of 1 to 1000 of resorcin have no appreciable influence on the rate of the heart-beat or the work done by that viscus, but that stronger solutions of the strength of 20 to 1000 reduced the rate and force and rapidly caused diastolic arrest. His conclusions are that in small doses it stimulates the heart, and in larger doses stops it in diastole. Beyer also asserts that it slows the pulse by acting on the peripheral vagi, a conclusion confirmed by our own studies. We can also endorse his assertion that small doses stimulate the heart, as we found that in the intact dog the dose of 0.0714 gram to the kilo had this effect.

Hydroquinone.

Like the meta compound, hydroquinone (para) has been used in medicine as an antipyretic, but its value in therapeutics is exceedingly limited. Given to a dog in the dose of 0.033 gram to the kilo by the jugular vein, the animal being free to run about, hydroquinone produces great staggering and convulsions, with a somewhat quickened respiration. After being convulsed for from two to three minutes gradual recovery occurs, the animal being almost as well as before after the lapse of 15 minutes. Later a renewal of the convulsions may take place. Along with the convulsions there is a marked exophthalmia and running movements, the convulsions being epileptiform. The blood is black and inky looking. When the dog is attached to the manometer and 0.166 gram to the kilo of his weight is injected into his jugular vein, the tracing becomes largely altered by reason of the convulsions which ensue, the pulse-rate is considerably increased, but the arterial pressure progressively falls until the drop equals about 70 mm. of mercury, and ultimately ends in death. When the dose is as large as 0.2 gram to the kilo the pulse becomes very slow, but is soon replaced by a stage of very rapid beating, which continues to death. The blood pressure rises about 20 mm. of mercury. The slowing of the pulse, which is seen after the use of 0.166 gram to the kilo, we have proved to be due to stimulation of the vagus nerves, since section of these nerves at once produces a rapid rate characteristic of vagal section in the normal animal. That this is not due in any way to the convulsions is proved by its occurrence in the curarised dog.

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[1] Archiv für Physiologie: Du Bois Reymond, 1879. Supplement Band, p. 61.

[2] American Journal of Medical Sciences, April, 1886.

The fall of arterial pressure noted after the use of 0.166 gram to the kilo is due to the slowing of the pulse, since it was at once removed by section of the pneumogastric nerves, and the rise of pressure seen on the administration of 0.2 gram to the kilo is due to the increased force of the heart-beat, which is remarkably increased at this time. Further than this, the changes in the blood so interfere with its function as to produce asphyxia, thereby causing a rise of pressure. Finally, when the rapid pulse of the second stage is present, the pressure is kept up by this rapid pulse for a time, but ultimately falls, owing to the gradual paralysis of the vaso-motor system by reason of the gradual increasing asphyxia due to the changes in the blood and to the depression of the respiratory centre directly or indirectly. The cause of the rapid pulse seen during the second stage is pneumogastric palsy of a peripheral type, as powerful stimulation of these nerves fails to control the heart in the least. The lethal dose is about 0.08 to 0.1 gram to the kilo of the dog's weight by the jugular vein.

In the studies made by Brieger[1] upon the frog he found that the dose of 0.005 gram to a 55-gram frog caused convulsions in one minute, death in four and one-half hours; that 0.01 gram to a larger frog caused death in two and one-half hours, and that doses below 0.005 gram to 55 grams of frog produced death in six hours, while still smaller ones caused a fatal result in eight and one-half hours, convulsions only coming on in two hours. Brieger also found in a rabbit that the dose of about 0.0166 gram to the kilo given by the stomach produced no symptoms. On the next day he gave the same animal about 0.0332 gram to the kilo, and in half an hour cramps came on in the extremities. Along with these symptoms there was dilatation of the blood-vessels and lowered blood pressure with slowing of the pulse, which was soft and smaller, sensibility remained intact, and the reflexes at first increased, but failed later on. When smaller doses were given, less violent convulsions came on, but the urine was dark and contained no free hydroquinone.

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[1] Loc. cit.

According to Beyer,[1] small doses of hydroquinone in the frog reduce the rate of the heart and the amount of work done, and larger doses paralyse the walls of the great veins, sinus and auricles in the order in which they are named, while the ventricle is affected but slightly. In the heart of the terrapin small doses of hydroquinone slightly increase the work done by the heart, but reduce the pulse-rate, while larger doses decrease both rate and work. The sinus and auricle are much the most affected, the ventricle being least depressed. It first causes a contraction, then a dilatation of the veins, capillaries and arterioles, the veins being most affected. When injected into the body, muscular twitchings come on. It depresses the action of the red blood corpuscles. The blood becomes purplish brown. The drug acts more on veins than on arteries. It slows the pulse by acting on peripheral vagi. 0.1 to 0.2 gram to 100 cc. water acting on a 280-gram frog paralyses the veins and almost completely paralyses the ventricle. Brieger states that it produces dilatation of arterioles and lowered blood pressure. Small doses decrease the rate slightly; the pulse becomes small and soft.

It will be seen, on examining the results reached in our research, that they are in accord with those of the experimenters who have already worked with these drugs, and it may not be out of place to state that in those points where the results are not identical, the discrepancy lies in the fact that Beyer used the isolated heart of the frog and terrapin. It will be noted first of all that Brieger and ourselves have found (ortho) pyrocatechin the most poisonous of the group, hydroquinone also acting almost but not quite as powerfully, and the meta compound or resorcin proving itself the weakest of all. Thus in our work the lethal dose of pyrocatechin was found to be about 0.04 or 0.05 gram to the kilo; with hydroquinone it was found to be about 0.08 to 0.1 gram to the kilo, while resorcin was fatal only when the dose rose as high as from 0.7 to 1 gram to the kilo. In Brieger's studies the lethal dose of pyrocatechin was found to be 0.005 gram to 55 grams in the frog, death occurring in two hours, while with hydroquinone the same dose in the same kind of animal was followed by death in four and one-half hours. If the dose of pyrocatechin and hydroquinone was 0.01 gram to 55 grams, death came on in two hours with the former, and in two and one-half hours in the latter. The lethal dose of resorcin in the frog Brieger found to be 0.01 gram to 55 grams of frog's weight, only after six hours. 0.005 gram would not kill. In the research of Beyer it was found that hydroquinone was much more powerful than resorcin. Thus Beyer found that when a solution of hydroquinone of the strength of 0.5 to 500 cc. of saline was passed through the heart of a terrapin of 940 grams weight, a good deal of effect was felt, whereas a solution of 1 gram to 500 cc. of saline produced no effect. Again, Beyer found that it only required 0.4 gram of hydroquinone to 55 cc. of saline to kill the heart, whereas as much as 1 gram to 55 cc. was necessary if resorcin was used. He made no studies of pyrocatechin.

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[1] American Journal of Medical Sciences, April, 1886.

Phloroglucin.

When phloroglucin in the dose of 0.66 gram to the kilo is injected into the jugular vein of a dog attached to a manometer, through the carotid artery, it produces slowing of the pulse-rate by many beats and a slight fall of arterial pressure, which was but transient and which returns to the normal after a few seconds. The fall of pressure is very evidently due to the injection of the drug. That the slowness of the pulse is not due to cardiac depression seems proved by the absence of a fall of pressure, and by the fact that the pulse-waves are much increased in force. Section of the vagi only partially restores the rate of the pulse, and the slowing would seem to depend upon peripheral stimulation of these nerves, since the rate after section is still slower than it was before the dose was given. The blood under these circumstances does not show much, if any, change.

If the dose be as large as 0.8 gram to the kilo in 80 cc. of water, the pulse in the course of two minutes becomes slower by as much as 20 or 30 beats a minute, and a very marked fall of arterial pressure amounting to 60 mm. of mercury occurs, which is reduced by one-half as soon as the heart is rid of the drug. The slowing of the pulse is persistent and is not removed in the slightest by cutting the vagus nerves, so that, with these doses, as with the smaller ones, the peripheral vagi are stimulated, the pulse-waves being very full and strong.

The lethal dose to the dog by the jugular vein is between 1.0 gram and 1.2 gram to the kilo of his weight. Under such circumstances, death is due to respiratory failure, the heart beating some minutes after respiration ceases. That the action of the drug is on the respiration is also proved by the fact that the rapid injection of the compound into the jugular does not injure the heart. Whether the poison acts on the respiratory centre or not we cannot state, since the changes produced in the blood are noteworthy. Unlike pyrogallol, which produces remarkably black blood, this compound seems to make it more of a red-brick color or reddish brown, at the same time making it grumous looking or as a strong mixture of water-color paints appears. No struggles or convulsions come on with lethal doses, the animal passes so quietly from life to death as to make careful examination by the experimenter necessary before he can be absolutely certain that death has occurred.

Pyrogallol.

This substance when injected into the jugular vein of a dog in the dose of 0.05 gram to the kilo causes a slight increase of blood-pressure, due probably to gradual asphyxia and a pulse-rate which is somewhat slowed. The blood becomes exceedingly black in appearance and looks as dark as ink. No other symptoms are noted. If the dose be 0.1 gram to the kilo, a progressive fall of arterial pressure occurs until it reaches the abscissa line of the tracing about 8 minutes after the administration of the dose. The pulse is slowed by nearly one-half at this time, but is fairly strong, considering the exceedingly low arterial pressure. The change in the blood under such a dose is extraordinary, and death is brought about by failure of respiration, which ceases two or three minutes before the heart stops beating. That the fall of arterial pressure is owing to a gradual asphyxia due to the altered blood is proved by the fact that artificial respiration in a curarised animal fails to maintain the pressure or put off death for any length of time. The lethal dose of pyrogallol by the jugular vein is from 0.08 to 0.1 gram to the kilo. There are no struggles whatever after poisonous doses, and no general symptoms, except those of weakness and intoxication with unconsciousness, appear.

The following summary shows the points of similarity and dissimilarity between these two substances. Both slow the pulse by vagal stimulation. Both change the appearance of the blood. Both kill by respiratory failure, direct or indirect. Pyrogallol is much the more poisonous, 0.05 gram to the kilo being equal to nearly 1 gram to the kilo of phloroglucin. Death from pyrogallol in the jugular vein is produced by from 0.08 to 0.1 gram to the kilo, from phloroglucin it is 1.0 to 1.2 gram to the kilo.

(*To be continued.*)

Contribution from the Chemical Laboratory of Clark University, Worcester, Mass.

ON TAUTOMERIC COMPOUNDS.

II.

BY J. U. NEF.

The striking resemblance of ethyl dioxyterephthalate and of ethyl dioxypyromellithate as well as of ethyl succino-succinate and of ethyl *p*-diketo-hexam-ethylenetetracarboxylate to ethyl acetoacetate and ethyl benzoylacetate, must become apparent to any one who has worked with these compounds. Just as in the case of ethyl acetoacetate, metallic sodium acts on these substances with evolution of hydrogen and formation of readily soluble and unstable sodium salts.

That in the case of ethyl acetoacetate the metal is bound to oxygen, thus, $CH_3-CO-Na=CH-CO_2C_2H_5$, has been made exceedingly probable by the recent experiments of Claisen.[1] Nevertheless, on treatment of this salt with alkyl iodides, products are formed which unquestionably have the alkyl group bound directly to carbon, $CH_3 - CO - CHR - CO_2C_2H_5$, and not to oxygen, $CH_3COR = CH - CO_2C_2H_5$, as might be expected. The decomposition products[1] of substituted aceto-acetic ethers as well as their behavior towards hydroxylamine and phenylhydrazine leave no room for doubt that the alkyl group is bound directly to carbon.

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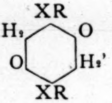
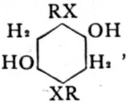
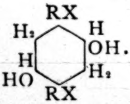
[1] Ber. d. chem. Gesell. **20**, 646, 651.

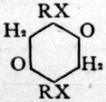
It was therefore of interest to determine whether the products formed by the introduction of alkyl as well as of acid radicals in the case of the above mentioned four compounds have the substituted radical (R) bound to carbon or to oxygen.

If, for instance, in the case of succino-succinic ether the alkyl group (R) is bound to carbon, 

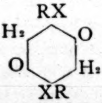
, the compound obtained must show the behavior of a ketone, *i. e.* it must form a hydrazone or oxime, and must easily be converted by reducing agents either into a phenol, 

, or secondary alcohol, 

. Furthermore, the above ketone formula admits of no chemical isomers, and of only two geometrical[2] isomers,

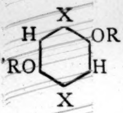


Cis-dialkyl derivative.



Trans-dialkyl derivative.

$(X = CO_2C_2H_5)$, which it must be possible to convert one into the other.

If, on the other hand, in the case of succino-succinic ether, the alkyl group is bound to oxygen,  H_2, there are six[1] distinct chemical isomers possible according to the position of the two hydrogen atoms, namely:

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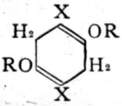
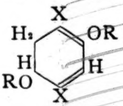
[1] Wislicenus, Ann. Chem. (Liebig) **186**, 187.

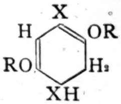
[2] v. Baeyer, Liebig's Annalen **245**, 169, 128.



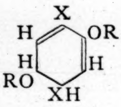
Δ 1, 4.



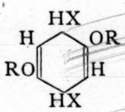
Δ 1, 3.



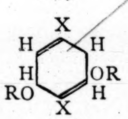
Δ 1, 5.



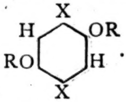
Δ 2, 6.



Δ 2, 5.



Δ 3, 6.

These isomers are all to be considered as dihydro-benzene derivatives, and by removal of the two hydrogen atoms must all give one and the same simple benzene derivative,  .

These isomers must also show the behavior of phenol ethers and not be acted upon by either hydroxylamine or phenylhydrazine. Further, they cannot by addition of more hydrogen be converted into bodies acting like phenols or secondary alcohols.

The study of the substitution-products of the four above mentioned substances has conclusively proved that in all of them the substituted group is bound to oxygen. Their behavior is entirely in harmony with the above theoretical deductions, and the proofs are especially convincing in the case of succino-succinic ether.

While only one dibenzyl-dioxyterephthalic ether was obtained, three simple isomeric and one polymeric dibenzyl succino-succinic ethers were obtained; also, whereas only one dibenzoyl-dioxyterephthalic ether was obtained, it was possible to isolate with certainty five isomeric dibenzoyl succino-succinic ethers; the latter are therefore to be regarded as dihydro-dibenzoyl-dioxyterephthalic ethers; they all give on treatment with bromine in carbon disulphide solution one and the same dibenzoyl-dioxyterephthalic ether.

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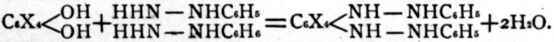
[1] There are more than six isomers possible if geometric isomers and isomers with para bonds be considered. The existence of the latter is, however, rendered exceedingly improbable by the work of v. Baeyer on the constitution of benzene, Ann. Chem. (Liebig) **245**, 112; ibid. **251**, 259.

These facts furthermore make it probable that ethyl succinosuccinate itself is also nothing but a dihydro-dioxyterephthalic ether, which also v. Baeyer[1] has recently considered probable. This substance, however, is still regarded as tautomeric, just as also acetoacetic ether, phloroglucin, and many others; *i. e.* it seems to show a twofold chemical behavior, sometimes acting like a phenol, then again as a ketone. In order to explain the behavior of such tautomeric substances the assumption has to be made that according to the reagent acting upon them, the hydrogen is bound either to carbon or to oxygen. Such an explanation has unquestionably much against it, and especially since it attacks the foundation of modern structural chemistry it is of the utmost importance that the most convincing proofs be brought forward to justify it.

Since Jeanrenaud[2] has explained the reaction which takes place when hydroxylamine acts upon ethyl succino-succinic ether, there is not a single reaction which is in favor of the ketone or hexamethylene nature of this substance, except that with phenylhydrazine.[3] This is no longer convincing, since also phenols with several electro-negative groups react with phenylhydrazine. In order to explain this reaction with phenols it is entirely unnecessary to make the assumption of a pseudo-form; the reaction simply takes place as follows:

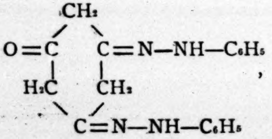


$$C_6X_4{<}\begin{matrix}OH\\OH\end{matrix} + \begin{matrix}HHN-NHC_6H_5\\HHN-NHC_6H_5\end{matrix} = C_6X_4{<}\begin{matrix}NH-NHC_6H_5\\NH-NHC_6H_5\end{matrix} + 2H_2O.$$

Phenol. Hydrazide.

Water is split off and a hydrazide formed.

The recent paper of v. Baeyer and Kochendoerfer[4] on the action of phenylhydrazine on phloroglucin is entirely in favor of this explanation. They did not obtain a hydrazone derivative,



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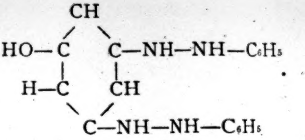
[1] Ann. Chem. (Liebig) **245**, 190.

[2] Ber. d. chem. Ges. **22**, 1283.

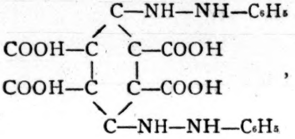
[3] Knorr and Bülow, Ber. d. chem. Ges. **17**, 2053.

[4] Ber. d. chem. Ges. **22**, 2189.

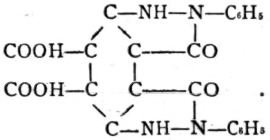
but a hydrazide,



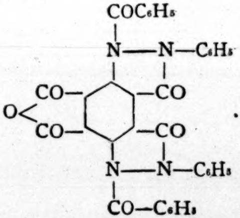
On the assumption of a pseudo-phloroglucin it is again necessary to assume a molecular rearrangement of a hydrazone to a hydrazide derivative. Furthermore, it has been proved that the reaction takes place in an analogous manner also in the case of another phenol, namely, hydroquinone-tetracarboxylic acid. There is formed at first a hydrazide,



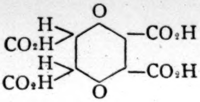
which instantly splits off water, giving the pyrazolon derivative,



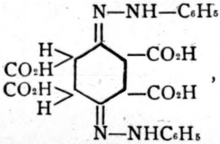
This substance is converted by benzoyl-chloride into a dibenzoyl derivative, and at the same time anhydride formation takes place,



In order to explain these facts by the assumption of tautomerism a twofold molecular rearrangement has to be assumed, first, that of a pseudo-form,

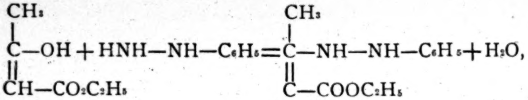


, second, that of a hydrazone,



, into a hydrazide, and this is hardly to be considered probable.

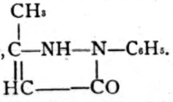
The above facts make it also probable that the pyrazolon derivatives as a whole cannot have the constitution last given them by Knorr.[1] The reaction, for instance, between phenylhydrazine and acetoacetic ether takes place as follows:



$$\begin{array}{l}CH_3\\ |\\ C-OH\\ \|\\ CH-CO_2C_2H_5\end{array} + HNH-NH-C_6H_5 = \begin{array}{l}CH_3\\ |\\ C-NH-NH-C_6H_5\\ \|\\ C-COOC_2H_5\end{array} + H_2O,$$

Hydrazide.

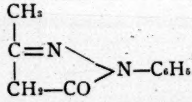
with the formation of a hydrazide, which then by splitting off alcohol passes into the pyrazolon derivative,



$$\begin{array}{l}CH_3\\ |\\ C-NH-N-C_6H_5.\\ \|\qquad\quad\ \ |\\ HC\text{——}CO\end{array}$$

By this formula the formation of antipyrine can be explained in a very simple manner, since by the action of methyl iodide the hydrogen of the imide group is simply replaced by methyl.

The explanation of Knorr[2] for the formation of antipyrine from 1-phenyl-3-methyl-5-pyrazolon,



, is far from probable.

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[1] Ann. Chem. (Liebig) **238**, 149.

[2] Ann. Chem. (Liebig) **238**, 207.

For this reason experiments have been begun with phenylhydrazine as well as pyrazolon derivatives of acetoacetic ether and of succino-succinic ether, in order to determine whether the reaction in reality does take place just as above with phloroglucin and hydroquinone-tetracarboxylic acid.

Succino-succinic ether, as well as ethyl dioxyterephthalate, are therefore not tautomeric compounds; they react solely as phenol-like bodies. The different physical modifications of these substances correspond in no way to the assumed desmotropic conditions given them by Hantzsch and Herrmann[1]; they are simply physical isomers. There are a vast number of organic compounds which crystallise in more than one modification, for instance, benzophenone, meta-dinitrobenzene, triphenylmethane, mandelic acid, and mercury diphenyl, where it is absolutely impossible that the different modifications correspond to chemically different compounds, and where even polymerism is excluded. Furthermore, in the course of the following investigation a number of substances have been discovered which appear in several crystalline forms, and where desmotropic conditions are entirely excluded. Thus, for instance, diacetyl succino-succinic ether crystallises in two different modifications (discovered by Dr. Muthmann); also ethyl β-benzoyl-dihydro-dioxyterephthalate appears in two, perhaps three, entirely distinct forms. In order to explain this by means of desmotropic conditions, the assumption would have to be made of a constant wandering of the benzoyl and acetyl group from oxygen to carbon and *vice versa*, which is furthermore entirely inconsistent with the chemical behavior of these substances.

The differences between the various forms in which a substance crystallises have unquestionably nothing to do with the chemical constitution, but are to be explained solely on physical grounds. The property of polymorphism is explained most simply by the different arrangement of the same molecules in the various crystalline forms.

The assumption of Hantzsch and Herrmann[2] that all benzene derivatives are colorless, while hydrogenated benzene derivatives are colored, is confuted by the following facts:

1. The diimido-derivative of ethyl *p*-diketo-hexamethylene-

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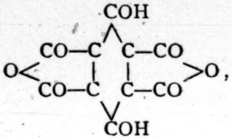
[1] Ber. d. chem. Ges. **20**, 1303, 2801; **21**, 1754.

[2] Ibid.

tetracarboxylate is a *perfectly colorless* substance, in every way analogous in chemical behavior to the diimido-derivative of succino-succinic ether.[1] This substance, whether it be regarded as a diamido or diimido derivative, is either a dihydro- or a hexahydro-benzene derivative, and should therefore, according to the hypothesis of Hantzsch and Herrmann, be colored.

2. The *yellow colored* acids, dioxyterephthalic and dioxypyromellithic acid, are *undoubtedly benzene* derivatives. Their great stability in comparison to succinylo-succinic acid[2] can only be explained in this way; furthermore, the instability of the carboxylated derivatives of benzoquinone[3] makes it probable that a carboxylated dihydro-quinone would be extremely unstable. Now, dioxypyromellithic acid on being heated to 300°-350° loses water and goes quantitatively into the dianhydride,



which can be distilled without decomposition. It is a deep dark yellow colored substance possessing a strong red fluorescence. On heating with acetic anhydride it is instantly converted into a colorless diacetyl derivative, which proves that it has two phenol hydroxyl groups, and therefore, *though strongly colored*, it is a *benzene derivative*. The salts of the hydroquinone dianhydride are *also colored deep red, almost black*.

3. The sodium salt of the primary methoxy-pyromellithic ether which crystallises in *yellow fluorescent plates*, and could be analysed, is a *benzene derivative*, $C_6\left\{\begin{array}{l}ONa\\ OCH_3\\ (CO_2C_2H_5)_4\end{array}\right.$, since on treatment with methyl iodide it is converted quantitatively into dimethoxy-pyromellithic ether, an unquestioned benzene derivative.

4. The disodic salt of dioxy-pyromellithic ether contains alcohol and is a reddish yellow substance. On driving off the alcohol, by

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[1] v. Baeyer, Ber. d. chem. Ges. **19**, 428.

[2] Herrmann, Ann. Chem. (Liebig) **211**, 321; v. Baeyer and Noyes, Ber. d. chem. Gesell. **22**, 2168.

[3] Ann. Chem. (Liebig) **237**, 1.

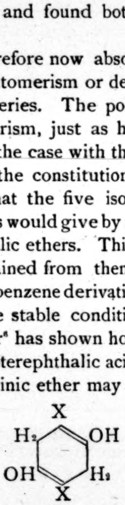
heating at 100°, it is converted into a *deep red powder* like vermilion. The substance is a *benzene derivative*, $C_6\begin{cases}(ONa)_2\\(CO_2C_2H_5)_4\end{cases}$, since by treatment with benzoyl or acetyl chloride it can be converted almost quantitatively into the corresponding ether, which is undoubtedly a benzene derivative.

The remarks of Hantzsch and Herrmann[1] about the salts of dioxyterephthalic ether and of diamidoterephthalic ether are also confuted by (3) and (4). Hantzsch and Herrmann[2] have put forward as the only chemical proof for desmotropism in the succino-succinic series, the fact that tetraoxyterephthalic ether and quinone-dioxyterephthalic ether give with hydroxylamine, oximes. I have already pointed out in my first paper on this subject[3] that these substances are not oximes, but oxyammonium salts. This supposition was found to be correct by Böniger,[4] who again analysed the substances and found both identical and to be an oxyammonium salt.

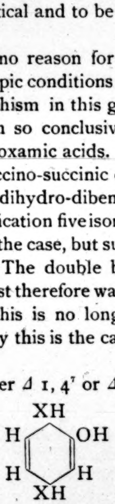
There is therefore now absolutely no reason for assuming the existence of tautomerism or desmotropic conditions in the succino-succinic acid series. The polymorphism in this group is due to physical isomerism, just as has been so conclusively shown by Lossen[5] to be the case with the hydroxamic acids.

As regards the constitution of succino-succinic ether, it might be expected that the five isomeric dihydro-dibenzoyl-dioxyterephthalic ethers would give by saponification five isomeric dihydro-dioxyterephthalic ethers. This is not the case, but succino-succinic ether was obtained from them all. The double bonds in these hydrogenated benzene derivatives must therefore wander and there exists only one stable condition. This is no longer surprising, since v. Baeyer[6] has shown how easily this is the case with Δ 2, 5, Δ 1, 5, dihydroterephthalic acid.

Succino-succinic ether may be either Δ 1, 4[7] or Δ 2, 5,



Δ 1, 4.



Δ 2, 5.

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[1] Ber. d. chem. Ges. **21**, 1754.

[2] Hantzsch and Zeeckendorf, Ber. d. chem. Ges. **20**, 2799, 2800.

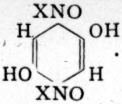
[3] This Journal **11**, 5.

[4] Ber. d. chem. Ges. **22**, 1289.

[5] Ann. Chem. (Liebig) **252**, 170.

[6] Ann. Chem. (Liebig) **251**, 290.

[7] v. Baeyer, Ann. Chem. (Liebig) **245**, 190.

dihydro-dioxyterephthalic ether. The Δ 2, 5 formula explains best the formation of dinitroso-succino-succinic ether,[1] which unquestionably has the two nitroso groups bound to the carbon atoms holding $CO_2C_2H_5$, 

. Furthermore, the corresponding dihydro-diamido-terephthalic ether (commonly known as the diimide of succino-succinic ether) belongs to the hexagonal trapezohedral, tetartohedral system,[2] and must therefore possess asymmetrical carbon atoms, which is only the case with the Δ 2, 5 formula.

Remarkable is the fact that succino-succinic ether, as well as *p*-diketo-hexamethylene-tetracarboxylic ether, cannot be further reduced, which must undoubtedly be the case if these substances ever appeared as ketones. Since *p*-diketo-hexamethylene-tetracarboxylic ether is very stable in alkaline solution, attempts were made to add hydrogen by means of long treatment with sodium amalgam, but without success. Experiments in acid solution with zinc dust gave the same negative results.

If the hypothesis be made that hydrogen adds itself only with great difficulty to a carbon atom containing the hydroxyl group, $-COH=$, in a closed chain of carbon atoms, the above fact is explained without difficulty, whether the resulting compound be regarded as a Δ 1, 4 or a Δ 2, 5 dihydro-derivative. It is then also no longer surprising that monoxy-terephthalic acid[3] takes up four hydrogen atoms and not two by treatment with reducing agents.

The above hypothesis is, however, only offered as a suggestion and little value is to be attached to it. The fact that *p*-dioxyterephthalic ether, as well as its acid and alcohol ethers, take up only two hydrogen atoms by reduction is beyond dispute.

The great resemblance of succino-succinic ether and of dioxyterephthalic ether to aceto-acetic ether makes it probable that also the last-named substance is a compound containing the hydroxyl group, $CH_3-COH=CH-CO_2C_2H_5$. This being the case, it ought also to form alkyl and acid ethers in which the substituted group (R) is bound to oxygen, $CH_3-COR=$

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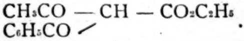
[1] Ann. Chem. (Liebig), **229**, 58.

[2] Muthmann, Zeitschr. für Kryst. **15**, 62.

[3] v. Baeyer and Tutein, Ber. d. chem. Gesell. **22**, 2178.

$CH - CO_2C_2H_5$; these ethers must then of course be insoluble in alkalies.

The experiments just begun with aceto-acetic ether with this object in view have given the following result: Sodic aceto-acetic ether,[1] when treated with one molecule of acetyl or benzoyl chloride, is converted partly into a product which is insoluble in alkalies. The yield, however, is very poor. 80 grams of sodic aceto-acetic ether give, when treated with benzoyl chloride, about 13 grams of a wine-yellow oil, insoluble in alkalies, besides very much mono-benzoyl-aceto-acetic ether,[2]



$$\begin{matrix} CH_3CO - CH - CO_2C_2H_5 \\ C_6H_5CO \nearrow \end{matrix}$$

.

The oil was purified as follows: To get rid of a slight amount of benzoyl chloride, it was allowed to stand with sodic hydrate for about ten hours, shaking thoroughly from time to time; traces of benzoic ether were driven over with steam, and then the residual oil again extracted with ether and washed with sodic hydrate; after distilling off the ether, previously dried with calcic chloride, there remained about 13 grams of oil. Attempts to distill it in a vacuum were fruitless, since decomposition takes place. It was therefore dried at 150° and analysed with the following result:

0.3422 gram substance gave 0.8908 gram CO_2 and 0.1615 gram H_2O.

	Theory for $\begin{matrix} (C_6H_5CO)_2 \searrow \\ CH_3 - CO \nearrow \end{matrix} C - CO_2C_2H_5$.	Found.
C	71.01	70.98
H	5.30	5.25

The substance is therefore to be regarded as a dibenzoyl-acetoacetic ether. Hitherto it has not been possible to introduce two acid radicals into the acetoacetic ether molecule, and the reaction in this case is best explained by the assumption of a disodium salt of acetoacetic ether. The oil is decomposed in the cold by alcoholic potash, concentrated sulphuric acid, and by bromine in chloroform solution. In all three cases about 0.8 gram to 1 gram of pure benzoic acid was obtained from 2 grams of the oil. The experiments with this substance, as well as with the product obtained by the action of acetylchloride upon sodic aceto-acetic ether, will be continued.

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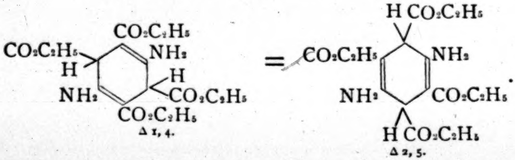
[1] Obtained by addition of sodium ethylate (free from alcohol) to aceto-acetic ether, diluted with an equal volume of absolute ether. The salt was dried on clay plates and washed with a small amount of ether, and then dried a short time at 100°.

[2] Bonne, Ann. Chem. (Liebig) **187**, 1; E. Fischer & Bülow, Ber. d. chem. Gesell. **18**, 2131.

EXPERIMENTAL PART.

Dihydro-diamido-pyromellithic ether,



On treating diamido-pyromellithic ether in alcoholic solution with zinc dust and dilute sulphuric acid, the chief product formed is para-diketo-hexamethylene-tetracarboxylic ether.[1] Besides this there is formed in small quantity an intermediate product,[2] which, since it is insoluble in caustic alkalies, can readily be separated from the main product. Diamido-pyromellithic ether is dissolved in as little hot alcohol as possible, a large excess of zinc dust, and then slowly dilute sulphuric acid (1 : 3) is added so as to cause a rapid evolution of hydrogen. As soon as the solution becomes colorless and a white crystalline precipitate begins to appear, a large amount of water is added and the mixture extracted with chloroform. The chloroform solution is washed with a 10 per cent. sodic carbonate solution, which takes up the saponified products, thereupon with dilute sodic hydrate, which extracts the diketone-compound with ease. The chloroform solution is washed with water and finally dried with calcic chloride; after distilling off the chloroform a white crystalline substance remains, which is difficultly soluble even in boiling alcohol, and crystallises therefrom in long fine needles, fusing at 212°.

0.1154 gram substance, dried at 110° and mixed with lead chromate, gave 0.2306 gram CO_2 and 0.0724 gram H_2O.

0.2015 gram substance, dried at 110°, gave 12.7 cc. nitrogen at 14° and 750 mm.

	Theory for $H_2C_6 \begin{cases} (NH_2)_2 \\ (CO_2C_2H_5)_4 \end{cases}$.	Found.
C	54.40	54.50
H	6.54	6.97
N	7.04	7.41

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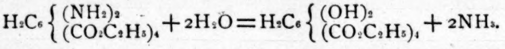
[1] Ann. Chem. (Liebig) **237**, 27.

[2] This Journal **11**, 7.

This same substance can also be obtained from para-diketo-hexamethylene-tetracarboxylic ether by melting with ammonic acetate.[1] The yield in this case is very poor, and it is necessary to treat repeatedly with ammonic acetate. The product finally dissolved in chloroform, and treated as above, was in every way identical with that obtained by reduction of diamido-pyromellithic ether.

Dihydro-diamido-pyromellithic ether is a perfectly colorless substance; in solution it is easily oxidised and then attains a reddish color. It is most readily soluble in chloroform. On dissolving in concentrated sulphuric acid and adding a small amount of water, it is instantly converted into para-diketo-hexamethylene-tetracarboxylic ether,

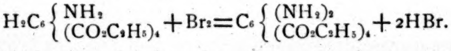


$$H_2C_6\left\{\begin{matrix}(NH_2)_2\\(CO_2C_2H_5)_4\end{matrix}\right. + 2H_2O = H_2C_6\left\{\begin{matrix}(OH)_2\\(CO_2C_2H_5)_4\end{matrix}\right. + 2NH_3.$$

The same ready elimination of the amido groups has been noticed by v. Baeyer in the case of the so-called diimido derivative of succino-succinic ether.

The stability of the imido groups in quinone diimido-pyromellithic ether,[2] where it is impossible under any condition to eliminate the nitrogen, is noteworthy in comparison with the abovementioned dihydro-diamido-benzene derivatives, and leads to the conclusion that they must be very differently constituted.

On treatment of dihydro-diamido-pyromellithic ether, dissolved in concentrated sulphuric acid, with one molecule of bromine,[1] it is converted quantitatively, with evolution of hydrobromic acid, into diamido-pyromellithic ether, as follows:



$$H_2C_6\left\{\begin{matrix}NH_2\\(CO_2C_2H_5)_4\end{matrix}\right. + Br_2 = C_6\left\{\begin{matrix}(NH_2)_2\\(CO_2C_2H_5)_4\end{matrix}\right. + 2HBr.$$

The substance therefore shows in every respect a perfectly analogous behavior to diimido-succino-succinic ether. Remarkable, however, in a high degree is the fact that the substance is perfectly colorless, while diamido-pyromellithic ether, on the other hand, is colored deep red. Heated with acetic anhydride it is converted into a colorless acetyl derivative, melting at 132°.

Pyrazolon Derivative of Dioxy-pyromellithic Acid.

On treating hydroquinone-tetracarboxylic ether in alcoholic solution at 100° with phenylhydrazine, there is formed, as I have already shown, a dipyrazolon derivative.[1] Since this substance is very difficult to obtain in a pure state in large quantities, I began experiments with the free acid. On adding phenylhydrazine to an aqueous solution of dioxy-pyromellithic acid, a substance separates out on cooling in yellowish colored prisms which is nothing but a phenylhydrazine salt of the acid. On heating, this is converted into the dipyrazolon derivative. In order to obtain this compound it is best, however, to proceed as follows: To a hot aqueous solution of dioxy-pyromellithic acid twice the calculated amount of phenylhydrazine hydrochloride is added, and to complete the reaction the mixture is heated on a water-bath for three to five hours. Very soon a yellow crystalline granular product begins to separate out which is hardly at all soluble even in boiling water. After repeated washing with hot water the substance was obtained pure, as shown by the following analyses:

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[1] v. Baeyer, Ber. d. chem. Ges. **19**, 428.

[2] This Journal **11**, 5.

I. 0.1534 gram substance dried at 180° gave 0.3434 gram CO_2 and 0.0502 gram H_2O.

II. 0.2000 gram substance dried at 180° gave 0.4474 gram CO_2 and 0.0624 gram H_2O.

III. 0.1316 gram substance dried at 180° gave 15 cc. nitrogen at 14° and 756 mm.

	Theory for $(CO_2H)_2C_6\left({NH \atop CO}>NC_6H_5\right)_2$.	Found. I.	Found. II.
C	61.38	61.03	61.00
H	3.25	3.63	3.50
N	13.06	13.48	...

The dipyrazolon compound, therefore, unquestionably is derived from the hydroquinone and not from the quinone, as Hantzsch[2]

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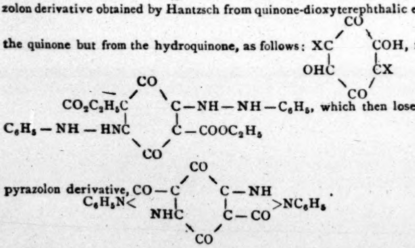
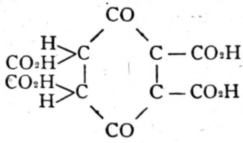
[1] This Journal **11**, 9.

[2] Ber. d. chem. Ges. **22**, 2845. For the same reason it is extremely probable that the pyrazolon derivative obtained by Hantzsch from quinone-dioxyterephthalic ether is derived not from the quinone but from the hydroquinone, as follows:



forms first a hydrazide, which then loses alcohol, forming the pyrazolon derivative.

When one considers that it has not as yet been possible to obtain a hydrazon derivative from believes, since a pyrazolon derivative containing two hydrogen atoms less requires only 2.80 per cent. hydrogen. The substance shows all the properties of a pyrazolon derivative; it dissolves in concentrated sulphuric acid, and on addition of water is precipitated unchanged; it dissolves in alkalies with deep purple coloration. The alkaline solutions, however, are readily oxidised, and on standing change in color to purplish red, reddish yellow, and finally to a stable yellow color showing a green fluorescence. The addition of an acid now precipitates a yellow amorphous flaky substance, which very likely is a compound containing two hydrogen atoms less, $\left[(CO_2H)_2C_6\left(\begin{matrix}N\\CO\end{matrix}>N.C_6H_5\right)_2\right]_x$. The same compound is obtained by oxidation of the alkaline solution with potassic ferricyanide, or better still by dissolving the pyrazolon derivative in fuming nitric acid and addition of water. The oxidation product is exceedingly stable; it can be boiled with alkalies without change, and even warm fuming nitric acid affects it but little.

The action of phenylhydrazine on hydroquinone-tetracarboxylic acid, it seems to me, can be explained best as follows: The assumption of a pseudo-modification, , is entirely unnecessary and, according to facts given in the theoretical introduction, is improbable. There is found at first a hydrazide, $(CO_2H)_2C_6\left\{\begin{array}{l}NH-NHC_6H_5\\COOH\\COOH\\NH-NHC_6H_5\end{array}\right.$, which then, by splitting off two molecules of water, goes into the pyrazolon derivative, $_2H)_2C_6\left\{\begin{array}{l}\begin{matrix}NH\\CO\end{matrix}>N.C_6H_5\\\begin{matrix}CO\\NH\end{matrix}>N.C_6H_5\end{array}\right.$, in which the two hydrogen atoms

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a para quinone, and further that in case of the other anilic acids it is the hydroxyl group that is affected by hydroxylamine (this Journal **11**, 21), it is extremely probable that the above explanation is the correct one.

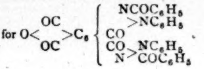
In this connection I would again call attention to the fact that hydroxylamine and phenylhydrazine are decomposed by quinone tetracarboxylic ether with formation of the hydroquinone. This action is so energetic that even *in the presence of much nitric acid* reduction takes place.

bound to nitrogen are replaceable by metals and also readily removed by oxidation.

This, and at the same time the constitution of the pyrazolon derivative itself, is proved by the behavior of the latter towards benzoyl chloride. On heating this substance in a flask with an excess of benzoyl chloride, much hydrochloric acid is evolved. If thereupon the excess of benzoyl chloride be removed by shaking with sodic hydrate, there remains a yellow acid anhydride insoluble in alkalies. It is better, however, to convert the benzoyl chloride by heating with alcohol into benzoic ether, whereupon the anhydride, on cooling, separates out in crystalline yellow flakes. Recrystallised once from hot alcohol, in which it is readily soluble, the substance gave the following results on analysis:

0.2067 gram substance dried at 110° gave 0.5271 gram CO_2 and 0.0705 gram H_2O.

Theory for

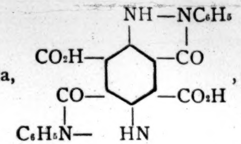


$$O<{}^{OC}_{OC}>C_6\left\{\begin{array}{l} \quad NCOC_6H_5 \\ \qquad >NC_6H_5 \\ CO \\ CO\quad NC_6H_5 \\ \quad N>COC_6H_5 \end{array}\right.$$

		Found.
C	69.68	69.54
H	3.23	3.78

It was possible to obtain good figures for carbon only by long ignition in a stream of oxygen, whereby the percentage of hydrogen found is somewhat high.

The dibenzoyl dipyrazolon anhydride melts at 140° to a viscous syrup, and volatilises without the slightest decomposition at a very high temperature. In solution, as well as in the solid state, it shows a green fluorescence. That the substance is an acid anhydride is proved by its behavior. After boiling an alcoholic solution with sodic hydrate, acids precipitate a yellow flaky substance which is readily soluble in alkalies, mild or caustic, and unquestionably represents the free acid while the benzoyl groups bound to nitrogen are not split off.

Benzoyl chloride has therefore acted on the dipyrazolon derivative as follows: first, the hydrogen atoms in the two imide groups are replaced by benzoyl, and at the same time anhydride formation has taken place between the two remaining carboxyl groups, which proves that the pyrazolon derivative cannot possess the other possible formula,  , since only phthalic acid, and not terephthalic acid, forms an anhydride.

Dioxypyromellithic acid is not affected by hydroxylamine under any other condition except the following: About ten times the calculated amount of hydroxylamine hydrochloride is added to a perfectly neutral solution of the potassium salt of the acid. After long boiling on a water-bath a yellow substance, crystallising in scales, separates out. It is completely insoluble in water and contains both potassium and nitrogen. On dissolving it in alkalies and pouring into a cold hydrochloric acid solution, a yellow granular product is precipitated which, on boiling with acids, is slowly converted into dioxy-pyromellithic acid.

The entire behavior of this substance proves that it is a hydroxamic acid like those obtained by Jeanrenaud[1] from acid ethers. It was therefore not further investigated.

Hydroquinone-tetracarboxylic Dianhydride, $(OH)_2C\left(\begin{smallmatrix}CO\\CO\end{smallmatrix}>O\right)_2$.

This substance is formed quantitatively by heating dioxy-pyromellithic acid for 10–15 minutes at 300°–350°. Water is given off in large amount, and finally at 350° the dianhydride begins to sublime. The deep yellow colored substance thus obtained is perfectly pure, as shown by analysis.

0.2187 gram substance gave 0.3866 gram CO_2 and 0.0182 gram H_2O.

	Theory for $(OH)_2C_6\left(\begin{smallmatrix}CO\\CO\end{smallmatrix}>O\right)_2$.	Found.
C	48.00	48.22
H	.80	.92

The dianhydride is volatile without decomposition. The best solvent for it is dry acetone or acetic ether. Crystallised from the last-named solvent, it was obtained in yellow prisms which show a strong red fluorescence. It is slightly soluble in ether; if a trace of water be present the sides of the test-tube become colored deep purple and blue. It dissolves in water at first with red color and yellowish red fluorescence; on standing or immediately on heating it goes over into dioxy-pyromellithic acid.

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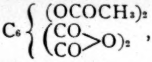
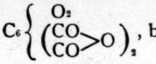
[1] Ber. d. chem. Ges. **22**, 1270.

On heating with acetic anhydride it dissolves at first, but almost immediately the diacetyl-derivative,  $C_6\left\{\begin{array}{l}(OCOCH_3)_2\\ \left(\begin{array}{l}CO\\CO\end{array}\!>O\right)_2\end{array}\right.$, separates out in colorless pearly scales, which are very difficultly soluble in alcohol and ether, and are only slowly attacked by boiling water. Boiling with alkalies, however, converts the diacetyl derivative into dioxy-pyromellithic acid. It melts at a high temperature, and is volatile without decomposition.

The salts of the hydroquinone dianhydride are deep dark red in color, almost black; the potassium and ammonium salts were easily obtained by means of alcoholic potash and ammonia. Many attempts were made with these salts, as well as with the dianhydride itself, to obtain by oxidation quinone-tetracarboxylic dianhydride,  $C_6\left\{\begin{array}{l}O_2\\ \left(\begin{array}{l}CO\\CO\end{array}\!>O\right)_2\end{array}\right.$, but without success.

On adding phenylhydrazine to an acetic ether solution of hydroquinone-tetracarboxylic dianhydride, there is formed at first a deep blue precipitate, which, on addition of more phenylhydrazine (in all 4 molecules), is converted into a yellow granular precipitate. Since this precipitate dissolves instantly in alkalies with yellow color and reddish fluorescence, and, on addition of acids, is precipitated again, the hydroxyl groups of the hydroquinone must have remained intact. The entire behavior of the product obtained shows that the anhydride groups have been attacked, and a product formed similar to those obtained by Hötte[1] with phthalic anhydride and phenylhydrazine.

Action of Halogens and of Nitric Acid on Dioxy-pyromellithic Acid.

On pouring bromine over hydroquinone-tetracarboxylic acid or its anhydride, not the slightest change is noticeable, even after many days. If, however, water be added, oxidation to the quinone and at the same time an evolution of carbonic anhydride take place. If the mixture be allowed to stand for twelve hours with an excess of bromine and some water, a yellow substance separates out in large quantity. Recrystallised from benzene, with addition of some alcohol, this was obtained in gold-yellow scales which melt at a high temperature and then sublime in scales. It coincides thus in its properties with bromanil.

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[1] J. prakt. Chem. **35**, 265.

0.1211 gram substance, dried at 110°, gave 0.0760 gram CO_2 and 0.0028 gram H_2O.

	Theory for $C_6Br_4O_2$.	Found.
C	16.98	17.12
H	...	.25

On treatment with caustic potash, it was converted into potassic bromanilate (obtained in long brownish red needles), and from it bromanilic acid was obtained with all its characteristic properties. The behavior of the bromanil towards nitrites[1] was studied, and potassic nitranilate obtained just as from chloranil. The potassium salt was converted into the barium, oxyammonium salt, as well as into nitranilic acid itself, and found to be in every way identical with the corresponding products from chloranil.

The bromanil was further converted by means of sulphurous acid in acetone solution into hydrobromanil. Recrystallised from acetic acid, this was obtained in long compact needles fusing at 246°.

A bromine determination according to the method of Carius gave the following results:

0.1361 gram substance, dried at 110°, gave 0.2428 gram AgBr or 0.1033 gram Br.

0.2951 gram substance, dried at 110°, gave 0.5202 gram AgBr or 0.2214 gram Br.

	Theory for $C_6Br_4(OH)_2$.	Found.	
		I.	II.
Br	75.17	75.90	75.02

The formation of bromanil from hydroquinone-tetracarboxylic acid takes place in two stages. At first quinone-tetracarboxylic acid, $C_6\left\{\begin{matrix}O_2\\(CO_2H)_4\end{matrix}\right.$, is formed. The carboxylated derivatives of benzoquinone are, as I have already shown in the case of durylic acid quinone,[2] very unstable, and the carboxyl group is readily replaced by other groups, for instance, the nitro group.

In the second stage of the reaction, therefore, the bromine successively replaces all four carboxyl groups in quinone-tetracarboxylic acid, and bromanil, $C_6Br_4O_2$, is thus formed. The yield of bromanil obtained is good; two grams acid gave regularly 1.1 gram bromanil.

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[1] Ber. d. chem. Gesell. **20**, 2027.

[2] Ann. Chem. (Liebig) **237**, 17.

On treatment of hydroquinone-tetracarboxylic acid with hydrochloric acid and potassic chlorate, there is likewise formed chloranil. The yield here too is a good one. The chloranil obtained was converted into hydrochloranil (fusing point found, 239°). It was also converted into potassic chloranilate and nitranilate. Since these substances, as well as the chloranil itself, were in every way identical with the corresponding products obtained from aniline, I deemed an analysis superfluous.

Iodine, potassium iodide and water do not act on hydroquinone-tetracarboxylic acid. On adding some iodic acid a violent reaction takes place, and a yellow substance is formed, which, however, is not iodanil, but iodoform.

From the above facts, and from the experience with durylic acid quinone, we should expect to obtain nitranil, $C_6(NO_2)_4O_2$, by the action of nitric acid on hydroquinone-tetracarboxylic acid. This, however, is not the case, but nitranilic acid is formed almost quantitatively. On adding hydroquinone-tetracarboxylic dianhydride in small portions to nitric acid (1.4) cooled to 0°, and then slowly adding an equal volume of water, nitranilic acid separates out in needles. It was purified according to the directions given in this Journal **11**, 18. The free acid, as well as the characteristic barium, sodium, potassium and oxyammonium salts, were compared side by side under the microscope with the corresponding products from chloranil, and found identical in every particular.

The above results with chlorine and bromine, as well as the results with durylic acid quinone, prove that unquestionably nitranil, $C_6(NO_2)_4O_2$, is at first formed. This substance, however, is extremely unstable, and immediately goes over into nitranilic acid, $C_6\left\{\begin{matrix}(NO_2)_2\\(OH)_2\\O_2\end{matrix}\right.$. I believe, therefore, that also by the action of nitrites on chloranil, nitranil is at first formed, but that it cannot be isolated.

A similar result was obtained by the action of potassic nitrite on quinone-dibromterephthalic ether. In this case also, not quinone-dinitro-terephthalic ether, but quinone-dioxy-terephthalic ether was obtained.

The above results confirm also the assumption of Nietzki and Preusser,[1] who found it necessary to suppose the intermediary formation of nitranil in order to explain the formation of nitranilic acid from meta-dinitro derivatives.

The behavior of dioxy-pyromellithic acid towards reducing agents is interesting. Many experiments carried on in acid and in alkaline solution showed that it was impossible to add hydrogen and at the same time prevent the splitting off of the carboxyl groups. The method by which para-dioxyterephthalic acid has been reduced[2] is here of no avail.

Also attempts to saponify dihydro-dioxypyromellithic ether (formerly called para-diketo-hexamethylene-tetracarboxylic ether), whether in alkaline or acid solution, proved that, notwithstanding all possible precautions, it was impossible to prevent the splitting off of the carboxyl groups as carbonic anhydride. The above ether, furthermore, is exceedingly stable in the presence of alkalies; it can, for example, be left in sodic hydrate solution for four days without much change.

These facts, as well as even more the results with succinosuccinic acid,[1] show how unstable hydrogenated hydroxylised benzene-carboxylic acids are. Under these circumstances the knowledge of the great stability of dioxyterephthalic acid, and still more of dioxypyromellithic acid, leads one to the inevitable conclusion that these are *colored benzene derivatives*, and that they *can never exist* as dihydroquinone-carboxylic acids.

Attempts to prove whether the substituted groups in Dioxy-pyromellithic and in Para-diketo-hexamethylene-tetracarboxylic Ether are bound to Carbon or to Oxygen.

The first experiments on this subject have already been published in this Journal, Vol. 11, p. 1. The behavior of dimethoxy-pyromellithic ether (melting point 95°) proves that the methyl groups in it are bound to oxygen, since it reacts neither with phenylhydrazine nor hydroxylamine, and is not affected by bromine. Later experiments show that it can be treated with zinc dust and acetic acid without any change. In order to prove that the substance is a phenol ether, the following experiment was carried out: 4 grams dimethoxy-pyromellithic ether (melting point 95°) were heated in dilute alcoholic solution with one and a half times the calculated amount of caustic soda. After evaporation of the alcohol, a white sodium salt was obtained which is little soluble in alcohol. A small portion was dissolved in water, and converted by means of lead acetate into the insoluble lead salt. This, after thorough washing, was decomposed by sulphuretted hydrogen, and the concentrated filtrate gave, on addition of concentrated hydrochloric acid, a colorless white substance, crystallising in needles, and exceedingly soluble in cold water. It in all probability is dimethoxy-pyromellithic acid. The main portion of the above sodium salt was converted into the colorless insoluble silver salt, which, treated with methyl iodide, gave in considerable quantity methyl dimethoxy-pyromellithate (melting point 134°), identical with the product described below. These facts prove conclusively that the methyl groups are bound to oxygen.

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[1] Ber. d. chem. Gesell. **20**, 799.

[2] v. Baeyer and Noyes, Ber. d. chem. Gesell. **22**, 2168.

Further, the intermediate product[1] obtained by the action of methyl iodide on disodic dioxy-pyromellithic ethyl ether was analysed. It crystallises from alcohol in beautiful yellow plates showing a strong green fluorescence.

0.2200 gram substance, dried at 110° and mixed with lead chromate, gave 0.4188 gram CO_2 and 0.1069 gram H_2O.

0.1122 gram substance dried at 110° gave on ignition with H_2SO_4 0.0183 gram Na_2SO_4.

	Theory for $C_6\left\{\begin{array}{l}ONa\\OCH_3\\(CO_2C_2H_5)_4\end{array}\right.$.	Found.
C	52.53	51.91
H	5.30	5.40
Na	5.30	5.29

The salt is but little soluble in water; the best solvent is alcohol, and the solution shows a greenish yellow fluorescence. It decomposes at high temperature without melting, and when treated with methyl iodide is converted quantitatively into dimethoxy-pyromellithic ether. On adding dilute sulphuric acid the salt is converted into a yellow oil which has a green fluorescence, is volatile without decomposition, and not acted upon by concentrated nitric acid. Sodic hydrate converts it back to the yellow sodium salt again, and it therefore must be $C_6\left\{\begin{array}{l}OH\\OCH_3\\(CO_2C_2H_5)_4\end{array}\right.$; it could under no condition be brought into the solid state.

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[1] This Journal **11**, 12.

The preparation of the sodium salts, especially of para-diketo-hexamethylene-tetracarboxylic ether, and of succino-succinic ether, can be accomplished with success only by following very definite conditions, just as in the case of acetoacetic ether.[1]

There is a great tendency in these compounds, because of the presence of double bonds, to form addition products with sodium ethylate. Furthermore, Claisen[2] has shown that acid ethers, $R-CO_2C_2H_5$, also form addition products with sodium ethylate whereby the carboxyl group is changed to an ortho derivative,

$$R-C\begin{cases}ONa\\OC_2H_5\\OC_2H_5\end{cases}.$$

If, for instance, a benzene solution of para-diketo-hexamethylene-tetracarboxylic ether be added to a benzene solution containing about ten times the calculated amount of sodium ethylate, no salt is precipitated at all, whereas this is the case if only the calculated amount (2 molecules) of sodium ethylate be present. On addition, however, of absolute ether, a white salt separates out which contains all the diketo compound used, and is readily soluble in water and reacts with bromine just as the disodic salt.[3] The analysis showed that it contains 27.02 per cent. of sodium, which proves that much sodium ethylate is present simply as an addition product.

The sodium salts can, however, be obtained tolerably well by the following method, which was employed in the case of all the sodium salts made:

The substance is dissolved in dry chloroform; the calculated amount of sodium (two atoms) dissolved in as little alcohol as possible, and the solution, after cooling, diluted with chloroform, and immediately poured into the chloroform solution of the substance, taking care to shake thoroughly. In this way there is always formed fully 85 per cent. disodic salt and very little mono-sodic salt. The salts come down mostly as gelatinous precipitates, very difficult to filter. They were dried on clay plates, and when air-dried they contain up to 20 per cent. crystalline alcohol, which in most cases was easily driven off by heating at 100° in an air-bath.

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[1] Wislicenus, Ann. Chem. (Liebig) **186**, **187**.

[2] Ber. d. chem. Gesell. **20**, 646.

[3] This Journal **11**, 17.

Methyl Dimethoxy-pyromellithate, $C_6\left\{\begin{matrix}(OCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right.$.

The disodium salt of methyl dioxy-pyromellithate is precipitated as a yellow granular crystalline powder. On drying at 90°, it loses its crystal alcohol and becomes deep cinnabar red in color. Over 85 per cent. of it is then $C_6\left\{\begin{matrix}(ONa)_2\\(CO_2CH_3)_4\end{matrix}\right.$, as shown by the yield of diacetyl derivative obtained from it with acetyl chloride (see below). It dissolves in water with yellow color and with green fluorescence. On heating it in a sealed tube with an excess of methyl iodide it is converted into the dimethoxy-derivative. After distilling off the excess of methyl iodide, dilute sodic hydrate is added, and the emulsion obtained extracted with chloroform, and this then dried with calcic chloride. There is left, after distilling off the chloroform, a white product, which, crystallised once from methyl alcohol, is obtained in colorless rhombic plates melting at 134°.

0.1552 gram substance gave 0.2951 gram CO_2 and 0.0720 gram H_2O.

	Theory for $C_6\left\{\begin{matrix}(OCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right.$.	Found.
C	51.89	51.86
H	4.87	5.16

The compound is volatile without decomposition; it is not acted upon by phenylhydrazine, hydroxylamine, or bromine. Long treatment with zinc dust in acetic acid solution is without effect. The solutions of the substance are colorless, and give no coloration with ferric chloride. Reduced in alcoholic solution with zinc dust and concentrated hydrochloric acid, it is converted into a hydrogenated benzene derivative, insoluble in alkalies, which was obtained as a colorless oil and could not be made to solidify.

Methyl Diacetyl-dioxy-pyromellithate, $C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right.$.

This substance is formed instantly in the cold on adding acetyl chloride to the above mentioned sodium salt. The yield obtained was always 75–85 per cent.

After extracting with chloroform, washing with alkalies, and evaporating the dried chloroform solution, the residue, crystallised once from methyl alcohol, was pure.

0.1276 gram substance, dried at 120°, gave 0.2378 gram CO_2 and 0.0516 gram H_2O.

	Theory for $C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right.$.	Found.
C	50.70	50.82
H	4.23	4.49

The diacetyl derivative is volatile without decomposition; it melts at 147°, and dissolves easily in hot methyl alcohol, crystallising therefrom in long silky needles. A chloroform solution of the substance is not affected by an excess of bromine, even on standing for many days. Concentrated sulphuric acid decomposes it instantly in the cold, with formation of acetic acid and dioxypyromellithic ether (melting point 207°). An alcoholic solution, treated with sodium ethylate, is converted into acetic ether and disodic dioxypyromellithic ether. The behavior of the compound is thus entirely that of an acid ether of a phenol. Although very unstable in alcoholic solution towards alkalies, it is stable towards concentrated hydrochloric acid, and therefore it was possible to convert it by reducing agents into a hydrogenated benzene derivative.

Methyl Dihydro-diacetyl-dioxypyromellithate,

$$H_2C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right..$$

The diacetyl-dioxy-pyromellithic ether is dissolved in as little hot methyl alcohol as possible, and an excess of zinc dust and concentrated hydrochloric acid is added slowly, so as to produce a very energetic evolution of hydrogen. In 5–10 minutes the reduction is completed. The solution is decanted from the zinc dust and poured into a large amount of water. After extracting with chloroform, washing first with sodic hydrate and then with water, the chloroform solution is dried with calcic chloride. The chloroform is then distilled off, and the residue obtained pure by repeated crystallisation from methyl alcohol.

0.1635 gram substance, dried at 110°, gave 0.3031 gram CO_2 and 0.0713 gram H_2O.

	Theory for $H_2C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right.$.	Found.
C	50.47	50.59
H	4.67	4.85

A dihydro-benzene derivative has therefore been formed, and it is impossible, even by repeated treatment with zinc dust and concentrated hydrochloric acid in alcoholic solution, to add more than two hydrogen atoms.

The substance is volatile without decomposition; it is dimorphous. Crystallised from a large amount of methyl alcohol (in which it is very much more difficultly soluble than the compound containing two hydrogen atoms less), it separates out, provided the solution is cooled slowly and without disturbance, in long needles. These are very unstable, and are easily converted into the stable or ordinary modification. This latter form is generally obtained by crystallisation from methyl alcohol as a porous, lustreless white powder, melting at 173°.

Concentrated sulphuric acid decomposes it in the cold into acetic acid and para-diketo-hexamethylene-tetracarboxylic ether (melting point 175°). Sodium ethylate (two molecules) saponifies it to acetic ether and the disodic salt of the diketo compound.

The substance dissolved in *anhydrous* ether is converted by the vapors of *dry* bromine (one molecule), notwithstanding all care, into dioxy-pyromellithic ether (melting point 207°) with evolution of hydrobromic acid. The nascent hydrobromic acid must therefore split off the acetyl groups as follows:

$$H_2C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2C_2H_3)_4\end{matrix}\right. + Br_2 = C_6\left\{\begin{matrix}(OCOCH_3)_2\\(CO_2CH_3)_4\end{matrix}\right. + 2HBr =$$

$$C_6\left\{\begin{matrix}(OH)_2\\(CO_2CH_3)_4\end{matrix}\right. + 2CH_3COBr.$$

That this actually is the case is proved by the study of the corresponding dibenzoyl derivative where the benzoyl groups, because more stable, are not split off.

Treated with concentrated nitric acid (1.4) in the cold, the dihydro-diacetyl compound is converted first into dioxy-pyromellithic ether and then into quinone-pyromellithic ether (melting point 208°). Para-diketo-hexamethylene-tetracarboxylic ether itself shows exactly the same behavior with nitric acid.

The *same dihydro-diacetyl derivative* is formed by treating the sodium salt of para-diketo-hexamethylene-tetracarboxylic ether with acetyl chloride. Reaction takes place instantly in the cold, and after extraction with chloroform, washing with alkalies, etc., as above, a colorless substance was obtained (yield 20–40 per cent.). Recrystallised from methyl alcohol, it was obtained in needles or as a porous white powder melting at 173°, and thus, as well as in its chemical properties, it is identical with the product obtained by reduction. Thereby it is conclusively proved that the substitution products of para-diketo-hexamethylene-tetracarboxylic ether have the substituted group (R) bound to oxygen, $H_2C_6\left\{\begin{matrix}(OR)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$, and that these are dihydro-benzene derivatives.

Dibenzoyl-dioxy-pyromellithic ether, $C_6\left\{\begin{matrix}(OCOC_6H_5)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$:

This compound is formed with a yield of 85–90 per cent. on treating disodic dioxy-pyromellithic ether with benzoyl chloride. It is, however, unnecessary to isolate the sodium salt. Ethyl dioxy-pyromellithate is dissolved in sodic hydrate and the solution shaken with benzoyl chloride.[1] The reaction is completed in five minutes, and the yield is 90 per cent. or over.

Recrystallised once from alcohol the product is pure.

0.2105 gram substance, dried at 110°, gave 0.4842 gram CO_2 and 0.0962 gram H_2O.

	Theory for $C_6\left\{\begin{matrix}(OCOC_6H_5)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	63.36	62.75
H	4.95	5.08

The dibenzoyl derivative crystallises from alcohol in rhombic colorless plates, melting at 157°. It can be obtained by crystallisation from acetic ether in transparent many-sided crystals, easily capable of goniometric measurement. It is not acted upon by concentrated nitric acid or on long standing with an excess of bromine in chloroform solution. Concentrated sulphuric acid saponifies it in the cold to benzoic acid and dioxy-pyromellithic ether. Alkalies in alcoholic solution also saponify it with formation of benzoic ether and the sodium salt of dioxy-pyromellithic ether. Reduced in alcoholic solution with zinc dust and hydrochloric acid, hydrogen is added and there is formed

Dihydro-dibenzoyl-dioxy-pyromellithic ether, $H_2C_6\left\{\begin{matrix}(OCOC_6H_5)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.

The method of preparation and purification of this substance is exactly like that described for the corresponding dihydro-diacetyl derivative. It crystallises from alcohol in long flat plates; from acetic ether in prisms, melting at 135°, and capable of goniometric measurement.

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[1] Udranzsky and Baumann, Ber. d. chem. Gesell. **21**, 2744.

0.2366 gram substance, dried at 110°, gave 0.5438 gram CO_2 and 0.1132 gram H_2O.

	Theory for $H_2C_6\left\{\begin{matrix}(COC_6H_5)_2\\(CO_2C_2H_5)_4\end{matrix}\right.$.	Found.
C	63.16	62.70
H	5.26	5.33

The substance is volatile without decomposition. It is a dihydro-benzene derivative, and it remains unchanged by long and violent treatment with zinc dust and hydrochloric acid (in alcoholic solution). Treated with 2 atoms of bromine in dilute carbon disulphide solution it is converted quantitatively, with evolution of hydrobromic acid, into dibenzoyl-dioxy-pyromellithic ether (melting point 157°). Concentrated sulphuric acid splits it in the cold into benzoic acid and para-diketo-hexamethylene-tetracarboxylic ether (melting point 143°). These two substances can easily be separated by means of hot water. A similar decomposition takes place with 2 molecules of sodium ethylate, forming benzoic ether and the sodium salt of the diketone compound.

This *same substance* now is formed on treating the sodium salt of para-diketo-hexamethylene-tetracarboxylic ether with benzoyl chloride. Noteworthy is the fact that no reaction takes place until the benzoyl chloride is heated to its boiling point.

The yield is a very good one: from 1 gram sodium salt, 0.6 gram pure dihydro-dibenzoyl derivative was obtained. The substance is identical in every way with the one obtained by reduction of dibenzoyl-dioxy-pyromellithic ether. The absolute physical identity is established by the following crystallographical results obtained by Dr. W. Muthmann:

Monoclinic system: $\beta = 52° 37'$.

$$a : b : c = 1.8824 : 1 : 2.5039.$$

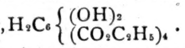
Planes: $r = (101) = -\text{Ᵽ}\infty$. $\rho = (\bar{1}01) = +\text{Ᵽ}\infty$. $a = (100) = +\mathrm{P}\infty$. $m = (110) = \infty \mathrm{P}$. $q = (011) = \text{Ᵽ}\infty$.

Elongation in the direction of the axis b. The ortho-pinacoid appears as a small plane. The clinodome is sometimes absent.

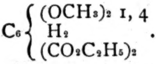
	Calculated.	Found.	
		Product from disodium salt.	Product obtained by reduction.
$m : m = (110) : (1\bar{1}0)$	... ...	112° 28′	... ...
$q : q = (011) : (0\bar{1}1)$	126° 38′	... ...	... ...
$a : q = (100) : (011)$	74° 11′	... ...	... ...

	Calculated.	Found.	
		Product from disodium salt.	Product obtained by reduction.
$a : r = (100):(101)$	22° 18′	... ...	22° ½′
$r : \rho = (101):(101)$	... ...	110° 0	110° 20′
$\rho : a = (\bar{1}01):(\bar{1}00)$	47° 42′	... ...	47° ½′
$m : r = (110):(101)$	59° 3′	58° 51′	... ...
$r : q = (101):(011)$	67° 11′	... ...	... ...
$q : m = (011):(\bar{1}10)$	53° 46′	... ...	... ...
$m : \rho = (\bar{1}10):(\bar{1}01)$	... ...	68° 2′	... ...
$\rho : q = (\bar{1}01):(011)$	85° 23′	... ...	... ...
$q : m = (011):(110)$	26° 35′	... ...	26° 22′

The crystals are colorless and transparent. The plane of the optic axes is parallel to the plane of symmetry. An optical axis appears at an angle not far from the perpendicular to one of the hemidome planes. Double refraction is medium. The identity of the two products is therefore proved."

The above results with the diacetyl and dibenzoyl derivatives prove that the substituted group is bound to oxygen, as well in case of dioxy-pyromellithic ether as also in the case of para-diketo-hexamethylene-tetracarboxylic ether. Since the ethers of the last-named substance show in every way an analogous behavior, it becomes very probable that this substance itself is nothing but a dihydro-dioxy-pyromellithic ether,  $H_2C_6\left\{\begin{array}{l}(OH)_2\\(CO_2C_2H_5)_4\end{array}\right.$.

Attempts to prove whether the substituted groups in dioxy-terephthalic ether and in succino-succinic ether are bound to oxygen or to carbon.

Dimethoxy-terephthalic ether, 

$$C_6\left\{\begin{array}{l}(OCH_3)_2\ 1,4\\H_2\\(CO_2C_2H_5)_2\end{array}\right..$$

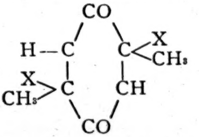
The disodic salt of dioxyterephthalic ether contains, dried in a desiccator, 20 per cent. of alcohol, and is colored reddish yellow. It is not possible to obtain it free from alcohol. On heating at 100° it is decomposed to a grayish powder. The presence of the alcohol, however, is not a hindrance in the preparation of the ethers.

Twenty grams were heated with an excess of methyl iodide in a sealed tube at 100° for six hours. After extracting with chloroform, washing with sodium hydroxide, etc., as with all the ethers, there were obtained 14.5 grams of pure dimethoxy-terephthalic ether, instead of 15.2 grams calculated. Recrystallised from alcohol, it was obtained in colorless rhombic plates melting at 101.5°, and volatile without decomposition.

0.2066 gram substance, dried at 110°, gave 0.4500 gram CO_2 and 0.1179 gram H_2O.

	Theory for $C_6\begin{cases}(OCH_3)_2\\H_2\\(CO_2C_2H_5)_2.\end{cases}$	Found.
C	59.57	59.39
H	6.38	6.34

This substance shows a remarkably strong blue-violet fluorescence, which is deceptive and might lead one to call the substance colored. Large transparent, easily measurable crystals from acetic ether show, however, not the slightest coloration under the microscope in polarised light (Dr. Muthmann). The solutions of the substance also show a marked blue-violet fluorescence, but give no coloration with ferric chloride.

These physical properties of the substance are so very remarkable, since all the other ethers, as well in the succino-succinic as in the para-diketo-hexamethylene-tetracarboxylic ether series, show not the slightest trace of fluorescence. I was for a long time inclined to ascribe the fluorescence to the presence of an impurity, but notwithstanding all efforts by chemical means, as well as repeated recrystallisation, it was impossible to eliminate or weaken the fluorescence. It might, however, be possible that in this case the methyl groups are bound to carbon, and therefore many varied experiments  were carried out with phenylhydrazine and hydroxylamine, but without success. The substance remains unchanged on long digestion with zinc dust and acetic acid. Its entire behavior thus shows that the methyl groups are bound to oxygen. On standing with bromine in chloroform solution, it is unchanged; on heating, however, to 100° in a sealed tube, hydrobromic acid is evolved and a colorless non-fluorescent product formed, which crystallises in needles and melts at 128°. On reducing in alcoholic solution with zinc dust and concentrated hydrochloric acid, hydrogen is added, and a colorless oil, insoluble in alkalies, is formed, which could not be made to solidify or be converted back into the original product.

Dimethoxy-terephthalic acid, $C_6\left\{\begin{array}{l}(OCH_3)_2\ 1, 4\\ H_2\\ (CO_2H)_2\end{array}\right.$.

The sodium salt of this acid is formed quantitatively from the ether by heating for half an hour in dilute alcoholic solution with sodium hydroxide. After driving off the alcohol, the solution is poured slowly into dilute hydrochloric acid, whereby the free acid separates out almost completely as a white powder. Recrystallised twice from hot water (four grams require about a liter of boiling water for solution), it was obtained in long colorless needles melting at 265°.

0.2318 gram substance, dried at 150°, gave 0.4512 gram CO_2 and 0.0936 gram H_2O.

	Theory for $C_6\left\{\begin{array}{l}(OCH_3)_2\\ H_2\\ (CO_2H)_2\end{array}\right.$.	Found.
C	53.10	53.08
H	4.42	4.53

Just as is the case with the ether, an aqueous solution of the acid shows a marked blue-violet fluorescence, which is not destroyed by mineral acids; ferric chloride causes not a trace of coloration, nor does it affect the fluorescence in the least. In the solid state, the acid, however, shows no fluorescence. Also the salts of the acid are colorless, and the solution of the ammonium salt shows no fluorescence. The silver salt is soluble in hot water, and crystallises therefrom in long, flat, radiating needles. The lead salt separates out in flakes, which quickly settle and transform themselves into a white granular powder.

Dibenzyl-dioxy-terephthalic ether, $C_6\left\{\begin{array}{l}(OCH_2C_6H_5)_2\ 1, 4\\ H_2\\ (CO_2C_2H_5)_2\end{array}\right.$.

Since by the reduction of dimethoxy-terephthalic ether, as well as from disodic succino-succinic ether and methyl iodide, oily products are obtained which cannot be made to solidify, experiments were undertaken with the benzyl ethers. On heating disodic dioxyterephthalic ether with an excess of benzyl chloride for about one to two hours with reversed condenser, reaction takes place. In order to be certain that no molecular rearrangement has taken place, an experiment was carried out with benzyl iodide, which reacts on the sodium salt at 100°. In both cases exactly the same compound is formed. When the reaction is completed the excess of benzyl chloride is distilled off by heating in a metal bath to 230°. The residue is extracted with chloroform, washed with sodium hydroxide, etc., and then recrystallised from alcohol, whereby it is separated from the benzyl chloride still left.

10 grams salt gave, when treated with benzyl chloride, 5 grams ether.

5 grams salt gave, when treated with benzyl iodide, 2.8 grams ether.

The product obtained with benzyl chloride is always colored slightly yellow; treated with zinc dust in acetic acid solution, it can, however, be obtained entirely colorless, as is the case directly with the product obtained by means of benzyl iodide. Recrystallised from alcohol, in which it is very easily soluble when hot, the ether is obtained in needles, melting at 96.5°.

0.2096 gram substance, dried at 110°, gave 0.5494 gram CO_2 and 0.1146 gram H_2O.

	Theory for $C_6\left\{\begin{matrix}(OCH_2C_6H_5)_2\\ H_2\\ (CO_2C_2H_5)_2\end{matrix}\right.$.	Found.
C	71.89	71.54
H	5.99	6.10

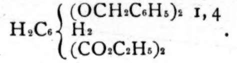
As the methyl ether this substance is colorless; it shows, however, a blue-violet fluorescence. The alcoholic solution also shows a marked blue-violet fluorescence, but it gives no coloration with ferric chloride. I am indebted to the kindness of Dr. W. Muthmann for the following description of the optical properties of this compound: "Needles, belonging to the monoclinic system, elongated in the direction of the axis of symmetry. The plane of the optic axes is perpendicular to the plane of symmetry, and forms with the normal to the predominant ortho plane a not very large angle. The acute bisectrix comes out at an angle through the mentioned predominant ortho plane (in sodium light). The axial angle is too great, so that the axes are not visible under the microscope."

The substance is volatile without decomposition; it is not acted upon by hydroxylamine or phenylhydrazine, or by reduction with zinc dust in acetic acid solution. The benzyl groups are stable in the presence of alkalies, so that on saponifying with alcoholic potash, a colorless acid, insoluble in water, is obtained which is probably dibenzyl-dioxy-terephthalic acid. In the presence of acids, however, the benzyl groups are less stable, and by boiling in alcoholic solution with concentrated hydrochloric acid the substance is converted into dioxy-terephthalic ether (melting point 133°).

Bromine, in chloroform solution, already attacks the substance in the cold with evolution of hydrobromic acid. A yellow substance crystallising from alcohol in flat needles, melting at 132°, was obtained, and it is probable that the bromine has attacked the benzyl groups, substituting the hydrogen atoms.

By reduction in alcoholic solution with zinc dust and concentrated hydrochloric acid, a dihydro-benzene derivative is formed, namely:

a-Dihydro-dibenzyl-dioxyterephthalic ether,



$$H_2C_6\left\{\begin{array}{l}(OCH_2C_6H_5)_2 \quad 1,4 \\ H_2 \\ (CO_2C_2H_5)_2\end{array}\right. .$$

The yield by the reduction is a very poor one, about 5 per cent., because of the instability of the benzyl groups in acid solution. It is essential to have a violent evolution of hydrogen and not to heat longer than five minutes, otherwise products, soluble in alkalies, are obtained, which are succino-succinic ether and dioxy-terephthalic ether.

After extracting with chloroform, washing with alkalies, etc., a product is obtained which is very difficultly soluble, even in boiling alcohol, and crystallises therefrom in colorless needles, melting at 169°; in solution these show a very weak blue-violet fluorescence, which cannot be removed.

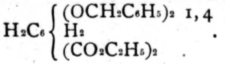
0.1677 gram substance, dried at 110°, gave 0.4404 gram CO_2 and 0.0994 gram H_2O.

	Theory for $H_2C_6\left\{\begin{array}{l}(OCH_2C_6H_5)_2 \\ H_2 \\ (CO_2C_2H_5)_2\end{array}\right.$.	Found.
C	71.56	71.62
H	6.42	6.62

The substance is volatile without decomposition; by boiling in alcoholic solution with concentrated hydrochloric acid, the benzyl groups are easily split off. It is also readily saponified by concentrated sulphuric acid in the cold. All attempts to remove the two hydrogen atoms of the dihydro-benzene derivative were fruitless.

It was now of interest to know whether this same product can be obtained from benzyl chloride and disodic succino-succinic ether.

β-, γ-, and π-Dihydro-dibenzyl-dioxyterephthalic ether,



$$H_2C_6\left\{\begin{array}{ll}(OCH_2C_6H_5)_2 & 1,4 \\ H_2 & \\ (CO_2C_2H_5)_2 & \end{array}\right. .$$

Disodic succino-succinic ether contains, dried in a desiccator, 20 per cent. of alcohol, which is detrimental for all reactions and must therefore be removed. This is possible in part by heating for half an hour at 100° or until 15 per cent. of the alcohol is driven off. It is impossible to drive off the remaining 5 per cent. of alcohol, since, as soon as this is accomplished, the salt burns up spontaneously. At first several portions were lost in this way. The sodium salt therefore, containing about 5 per cent. of alcohol, was used in all reactions carried out with this salt.

On treating the salt with benzyl chloride, reaction takes place only on heating to the boiling point of the benzyl chloride; with benzyl iodide, however, reaction takes place at 100°. In both cases identical products are obtained, and the preparation and purification is exactly the same as with benzyl-dioxy-terephthalic ether (*q. v.*). There is formed a colorless product insoluble in alkalies, which crystallises from alcohol in needles melting at 128°. This was at first regarded as a perfectly homogeneous substance, entirely different from the two isomeric β- and γ-derivatives obtained from it and described below. Dr. W. Muthmann, however, proved by an optical investigation that the above product, melting at 128°, is only a mixture of β-dihydro-dibenzyl-dioxy-terephthalic ether (melting point 148.5°) and of γ-dihydro-dibenzyl-dioxy-terephthalic ether (melting point 140.5°), which two substances furthermore are remarkably alike in appearance. The mixture of the two isomers shows naturally a lower melting point than either of the constituents. It was thereupon found possible to separate the isomers, since the β-isomer is less soluble in alcohol. By repeated recrystallisation from much alcohol, whereby only the crystals first separating out were collected, the β-isomer was obtained pure and perfectly homogeneous, and melting at 148.5°.

This substance was first obtained from the above mixture by violent sublimation, whereby the lower melting γ-isomer is decomposed by preference.

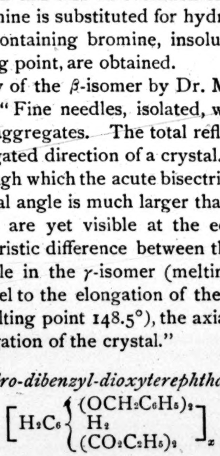
0.1289 gram substance dried at 110° gave 0.3353 gram CO_2 and 0.0770 gram H_2O.

	Theory for $H_2C_6\left\{\begin{array}{l}(OCH_2C_6H_5)_2\\ H_2\\ (CO_2C_2H_5)_2\end{array}\right.$.	Found.
C	71.56	71.03
H	6.42	6.67

The substance treated for a long time in alcoholic solution with zinc dust and hydrochloric acid is not further reduced, and is in great part recovered unchanged. Phenylhydrazine and hydroxylamine do not react on it. It is also not possible to remove the two hydrogen atoms in the dihydro-benzene derivative by oxidation: nitrogen trioxide passed in large excess into a chloroform or alcoholic solution of the substance leaves it unchanged. Similar negative results were obtained with chromic acid in acetic acid solution. Bromine in carbon bisulphide solution, which so readily converts the corresponding benzoyl and acetyl ethers into benzene derivatives, causes in this case an evolution of hydrobromic acid, but very likely bromine is substituted for hydrogen in the benzyl groups; products containing bromine, insoluble in alkalies, and having a low melting point, are obtained.

The optical study of the β-isomer by Dr. Muthmann gave the following results: "Fine needles, isolated, with no tendency to collect together in aggregates. The total reflection is sharp and parallel to the elongated direction of a crystal. A pinacoid plane predominates, through which the acute bisectrix comes out perpendicularly. The axial angle is much larger than in the case of the γ-isomer: the axes are yet visible at the edges of the field of vision. A characteristic difference between the two isomers lies in the fact that while in the γ-isomer (melting point 140.5°) the axial plane is parallel to the elongation of the crystal, in the case of the β-isomer (melting point 148.5°), the axial plane lies perpendicular to the elongation of the crystal."

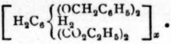
π-Dihydro-dibenzyl-dioxyterephthalic ether,



$$\left[H_2C_6\left\{\begin{array}{l}(OCH_2C_6H_5)_2\\ H_2\\ (CO_2C_2H_5)_2\end{array}\right.\right]_x.$$

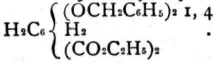
By dissolving the β-isomer just described in concentrated sulphuric acid in the cold, it is converted into a polymer which crystallises finely. For its preparation, however, it is better to take the above-mentioned mixture of β- and γ-isomers, melting at 128°, whereby the γ-isomer, which is not affected, can also be obtained pure. This is dissolved in concentrated sulphuric acid, and after standing in the cold for about ten minutes, poured into water, extracted with chloroform, washed with alkalies, etc. There remains after distilling off the chloroform a mixture of about 75 per cent. γ-isomer and 25 per cent. polymer. Since only traces of the polymer dissolve in boiling alcohol, while the γ-isomer is very soluble therein, a separation is readily possible. The polymer was treated repeatedly with hot alcohol, and finally recrystallised from acetic acid, from which solvent it was obtained in large colorless, measurable crystals, which often look like octahedra or dodecahedra.

0.1840 gram substance, dried at 140°, gave 0.4795 gram CO_2 and 0.1060 gram H_2O.

	Theory for  $\left[H_2C_6\left\{\begin{matrix}(OCH_2C_6H_5)_2\\H_2\\(CO_2C_2H_5)_2\end{matrix}\right.\right]_x$.	Found.
C	71.56	71.08
H	6.42	6.40

The substance melts at 272° and is volatile without change, but at a much higher temperature than the α-, β- and γ-isomers, whereby, as well as because of the difficult solubility in all solvents except hot acetic acid, the fact that the substance is a polymer is unquestionable.

γ-Dihydro-dibenzyl-dioxyterephthalic ether,



$$H_2C_6\left\{\begin{matrix}(OCH_2C_6H_5)_2\ 1,4\\H_2\\(CO_2C_2H_5)_2\end{matrix}\right..$$

This substance is formed together with the β-isomer by treating disodic succino-succinic ether with benzyl chloride or iodide. The alcoholic mother-liquors, from which the β-isomer has been removed, contain the γ-isomer, but it is very difficult to obtain the latter free from β-isomer, by fractional crystallisation from alcohol. The solutions, from which the β-isomer has been in part removed, are therefore evaporated, and then dissolved in concentrated sulphuric acid. Or the above mixture of β- and γ-isomers, melting at 128°, obtained directly from disodic succino-succinic ether, is dissolved in concentrated sulphuric acid. The β-isomer is thus polymerised, while the γ-isomer remains unchanged. Since hot alcohol readily takes up the γ-isomer, whereas the polymer dissolves only in traces, a separation is now accomplished with ease. From the alcoholic solution on concentration the γ-isomer is obtained in long, lustreless needles, grouped together in sheaves, and melting at 140.5°.

0.2121 gram substance, dried at 110°, gave .05538 gram CO_2 and 0.1270 gram H_2O.

	Theory for $H_2C_6\begin{cases}(OCH_2C_6H_5)_2\\H_2\\(CO_2C_2H_5)_2\end{cases}$.	Found.
C.	71.56	71.21
H	6.42	6.65

The substance is volatile without decomposition; it does not react with phenylhydrazine or hydroxylamine, nor is it changed by long reduction with zinc dust and hydrochloric acid in alcoholic solution. In its behavior towards nitrogen trioxide, chromic acid and acetic acid, and also towards bromine, it is entirely analogous to the β-isomer (*q. v.*).

The optical results of Dr. Muthmann are as follows: "Needles, which have a great tendency to collect in fibrous asbestos-like aggregates. Isolated crystals have predominating a plane through which an acute bisectrix comes out perpendicularly. The axial angle is very small, at most 5°, so that the crystals, like isotropic bodies, remain dark in parallel light with crossed Nicols. The axial plane is parallel to the elongation of the crystal, and is exactly perpendicular to the predominating plane."

On treatment of disodic succino-succinic ether with benzyl chloride or iodide, two isomeric compounds are formed, both of which show the behavior of alkylated phenol ethers. The fact that the β-isomer polymerises so easily is a proof that it contains doubly bound carbon atoms.

The fact that the so-called α-dihydro-dibenzoyl-dioxy-terephthalic ether obtained by reduction of dibenzyl-dioxy-terephthalic ether, is not identical with either of the products obtained from succino-succinic ether, is not surprising, since six isomeric dihydro-benzene derivatives are possible (see introduction).

The study of the acid ethers of dioxyterephthalic ether and of succino-succinic ether has led to results which are even more conclusive, if that is possible, than those obtained with the alkyl ethers.

10 grams disodic dioxy-terephthalic ether gave with acetyl chloride, 7 grams (calculated 9 grams) of pure diacetyl derivative, melting at 154°, and identical with the product obtained by Wedel.[1] This substance is not acted upon by an excess of bromine, even after long standing in chloroform solution. It is split into its constituents by sulphuric acid in the cold.

10 grams disodic succino-succinic ether gave with acetyl chloride 2.5 grams (calculated 11 grams) diacetyl derivative, melting at 169°, and identical with Wedel's product.[1] It is very unstable, and even by recrystallisation from alcohol it is slowly decomposed into acetic ether and succinylo-succinic ether: it is insoluble in alkalies. Bromine converts it in chloroform solution into dioxy-terephthalic ether (cf. page 404), with evolution of hydrobromic acid. These results are entirely in accordance with those obtained in the pyromellithic acid series. Remarkable, however, to a high degree is the fact that diacetyl-dioxy-terephthalic ether and diacetyl-succino-succinic ether form crystals from acetic ether, which show not the slightest difference by a most careful inspection, and even the goniometrical results show a most remarkable resemblance. Were it not for the difference in melting point (15°), and total difference in chemical behavior towards bromine, the substances might be regarded as identical.

The following results were kindly given me by Dr. W. Muthmann:

"Diacetyl-dioxy-terephthalic ether, melting point 154°, monoclinic system.

$$a : b : c = 1.9292 : 1 : 1.2037, \beta = 71° 1'.$$

Diacetyl-succino-succinic ether, melting point 169°, monoclinic system.

$$a : b : c = 1.9814 : 1 : 1.2225, \beta = 69° 39\tfrac{1}{2}'.$$

Planes the same for both: $m = (110) = \infty P$; $c = (001) = 0P$; $\rho = (\bar{1}01) = +\bar{P}\infty$; $\omega = (\bar{1}11) = +P$.

The fundamental angles are as follows:

	Diacetyl-dioxy-tereph. Ether.	Diacetyl-succino-succ. Ether.
m : m	122° 32′	123° 25′
m : c	81° 0′	80° 31′
c : ρ	63° 17′	63° 44′

Thereby the complete isomorphism of the two substances is proven."

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[1] Ann. Chem. (Liebig) **219**, 81, 85.

These facts show how much some dihydro-benzene compounds resemble in physical respects the corresponding benzene derivatives. They are isomorphous, and can therefore form isomorphous mixtures with one another.

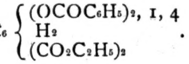
A similar observation has been made by Dr. Muthmann in the study of the dihydro-terephthalic acids of v. Baeyer,[1] and his results have been published in Groth's Zeitschrift für Krystallographie, Band 17, p. 460.

Furthermore, also benzoyl dioxy-terephthalic ether (melting point 174°) and *a*-benzoyl-succino-succinic ether (melting point 165°) show a like remarkable resemblance one to the other, and also form isomorphous mixtures with one another.

The fact that diacetyl and *a*-dibenzoyl-succino-succinic ether are dihydro-benzene derivatives is unquestionably proved by what follows.

In view of the isomorphism existing between the above-mentioned benzene and dihydro-benzene derivatives, the fact that succino-succinic ether itself, which is now to be regarded as a dihydro-dioxy-terephthalic ether (Δ 1, 4 or Δ 2, 5), forms isomorphous mixtures[2] with dioxy-terephthalic ether and other hydroxylated benzene derivatives is no longer surprising.

Dibenzoyl-dioxyterephthalic ether,



$$C_6 \begin{cases} (OCOC_6H_5)_2,\ 1,\ 4 \\ H_2 \\ (CO_2C_2H_5)_2 \end{cases}.$$

Benzoyl chloride acts instantly on disodic dioxyterephthalic ether, but in order to make the benzoyl derivative it is better simply to dissolve dioxyterephthalic ether in sodium hydroxide and to shake with benzoyl chloride.[3] In this way 20 grams were converted quantitatively into the benzoyl derivative, which recrystallised once from alcohol is pure.

0.2150 gram substance, dried at 110°, gave 0.5272 gram CO_2 and 0.0966 gram H_2O.

	Theory for $C_6 \begin{cases} (OCOC_6H_5)_2 \\ H_2 \\ (CO_2C_2H_5)_2 \end{cases}$.	Found.
C	67.53	66.88
H	4.76	4.98

The substance is difficultly soluble, even in boiling alcohol

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[1] Ann. Chem. (Liebig) **251**, 285.

[2] O. Lehmann, Zeitschr. für phys. Chemie **1**, 16.

[3] Udransky and Baumann, Ber. d. chem. Ges. **21**, 2744.

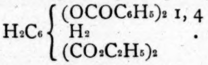
(about seven grams dissolve in a liter), and crystallises therefrom in long colorless needles, melting at 174°. The solutions are colorless, and show no fluorescence or coloration with ferric chloride. The substance volatilises without decomposition, and is not affected in the least on long standing in chloroform solution with bromine. Concentrated sulphuric acid splits it into benzoic acid and dioxyterephthalic ether, while two molecules of sodium ethylate in alcoholic solution decompose it into benzoic ether and disodic dioxyterephthalic ether.

Exactly as in the case of dibenzoyl-dioxy-pyromellithic ether, the benzoyl groups are stable in alcoholic solution towards hydrochloric acid, so that it is possible by reduction to obtain hydrogenated benzene derivatives. In this way in all five isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers were obtained which show an entirely analogous behavior.

Reduction with Aqueous Hydrochloric Acid.—Five grams dibenzoyl-dioxy-terephthalic ether were very finely pulverised and dissolved in as little boiling alcohol as possible (about 750 cc.), and then much zinc dust and concentrated hydrochloric acid added, in order to produce a very violent evolution of hydrogen. After about 15 minutes the reduction is complete, since repeated treatment of the reduction products thus obtained for 15 minutes longer did not show the slightest difference in the composition of the reduced products. The alcoholic solution is now poured into a large amount of water, and then extracted with chloroform and washed with sodium hydroxide, etc. Thus always about 2.5 grams of reduction-product were obtained, which proved to be a mixture of three isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers, and the separation of these could be accomplished very sharply.

Since one of the three isomers thus obtained is also formed directly from disodic succino-succinic ether, it will be advantageous to describe its preparation here.

α-Dihydro-dibenzoyl-dioxy-terephthalic ether,



$$H_2C_6\left\{\begin{array}{ll}(OCOC_6H_5)_2 & 1,4\\ H_2 & .\\ (CO_2C_2H_5)_2 & \end{array}\right.$$

Disodic succino succinic ether reacts even at ordinary temperature with benzoyl chloride, and the reaction is completed by gentle heat on a water-bath. After treatment with chloroform, sodium hydroxide, etc., 4.5 grams pure dibenzoyl derivative are obtained from 10 grams of the salt. It crystallises from alcohol in long colorless needles, melting at 165°, which show a remarkable resemblance to dibenzoyl-dioxy-terephthalic ether, and forms isomorphous mixtures with it. The first named substance is, however, much more easily soluble in hot alcohol.

0.2118 gram substance, dried at 110°, gave 0.5205 gram CO_2 and 0.1007 gram H_2O.

	Theory for $H_2C_6\left\{\begin{array}{l}(OCOC_6H_5)_2\\ H_2\\ (CO_2C_2H_5)_2\end{array}\right.$	Found.
C	67.24	67.02
H	5.17	5.28

The substance remains unchanged when treated for 15 minutes in alcoholic solution with zinc dust and concentrated hydrochloric acid, and from 0.5 gram substance taken, 0.3 gram pure substance, melting at 165°, was recovered. It is volatile without decomposition. Concentrated sulphuric acid splits it in the cold into benzoic acid and succino-succinic ether. The succino-succinic ether contains in this case always traces of dioxyterephthalic ether, which forms isomorphous mixtures with it. The same observation was made in splitting diacetyl-succino-succinic ether (melting point 169°) with concentrated sulphuric acid (cf. page 416). In both cases, therefore, a slight oxidation takes place on saponification.

The α-dibenzoyl-derivative remains unchanged on treatment with an excess of nitrogen trioxide in alcoholic or chloroform solution. Chromic acid in acetic acid solution completely destroys one portion, while much unchanged substance is recovered. It is, however, possible to remove the two hydrogen atoms by treating the substance in dilute carbon bisulphide solution with exactly the calculated amount of bromine (2 atoms). There is formed quantitatively, with evolution of hydrobromic acid, dibenzoyl-dioxy-terephthalic ether, melting at 174°, and on saponifying it with concentrated sulphuric acid pure dioxyterephthalic ether melting at 133° was obtained.

β- and γ-Dihydro-dibenzoyl-dioxy-terephthalic ether,

$$H_2C_6\left\{\begin{array}{l}(OCOC_6H_5)_2\ 1,4\\ H_2\\ (CO_2C_2H_5)_2\end{array}\right. .$$

The above mixture of α-, β-, and γ-dihydro-dibenzoyl-dioxy-terephthalic ethers can be separated as follows: 3 grams are dissolved in about 150 cc. alcohol, and subjected to fractional crystallisation. The least soluble fractions give finally (in very small quantity in comparison to the other two isomers present) a substance, crystallising in needles, which, by repeated recrystallisation, shows the constant melting point 165°, and in its entire behavior is identical with the above-described α-dihydro-dibenzoyl-derivative obtained from succino-succinic ether. The fractions more soluble in alcohol show the presence of two isomers, the one crystallising in spheres composed of an aggregation of needles, the other, in long, flat needles. The difference in solubility is very slight; sometimes crystals separate from a saturated solution, which consist entirely of one form only, but this is a matter of chance. Finally the following method of separation was found to be exceedingly sharp. The mixture of β- and γ-isomers is dissolved in as little warm ether as possible, and then a small amount of petroleum ether (boiling point 33°–50°), wherein the products are insoluble, added. On cooling, or standing in a flask without disturbance, transparent cubes, rectangular plates, and long, flat needles which have the ends cut off obliquely and are often grown into one another, separate out. These can be separated mechanically with ease, and often once crystallised, and thus separated were perfectly pure. It is generally necessary, however, to recrystallise the portions separated mechanically from ether with addition of a little petroleum ether, and again separate mechanically the portions that crystallise out. The concentrated ethereal filtrates give new crops of crystals again; it is important to see to it that a complete evaporation of the mother-liquor over the crystals never takes place. In this way the above transparent cubes, constituting what has been named the β-isomer, are obtained with a sharp melting point 138°: they remain unchanged by sublimation or repeated recrystallisation or by treatment in alcoholic solution with reducing agents, zinc dust and hydrochloric acid. The β-isomer is dimorphous, crystallising not only in cubes, but also in rectangular plates (mentioned above), which, however, represent the less stable modification.

0.1464 gram substance, dried at 110°, gave 0.3596 gram CO_2 and 0.0698 gram H_2O.

	Theory for $H_2C_8\left\{\begin{array}{l}(OCOC_6H_5)_2\\ H_2\\ (CO_2C_2H_5)_2\end{array}\right.$	Found.
C	67.24	66.99
H	5.17	5.29

The substance crystallises from ether or carbon disulphide in cubes or in long, rectangular plates. The latter represent the less stable modification, and heated, they undergo at 110° a change, becoming turbid and melting on higher heat sharply at 138°, just as the cubes. From alcohol the β-isomer was generally obtained in small spheres consisting of needles, owing to the fact that the substance separates out at first in oil globules. Once it was obtained in long, glistening needles.

For the following account of the optical properties of the substance I am indebted to the kindness of Dr. Muthmann. "*Cubes:*—Perfectly transparent crystals. 1 plane with diagonal extinction; 2 plane with parallel extinction. Through the first plane a bisectrix, but no axes, appears. Recrystallised from carbon disulphide on an object-glass, the cubes give a mixture of cubes and of rectangular plates (the latter predominating).

"*Rectangular plates:*—An acute bisectrix comes out almost perpendicularly through the principal plane. The axial angle is not very large; the double refraction medium. Both axes readily seen. The plane of the optic axis is perpendicular to the elongation of the crystal."

The β-isomer is converted, on treatment with concentrated sulphuric acid in the cold, into benzoic acid (melting point 120°) and succino-succinic ether (melting point 127°). On dissolving in much carbon disulphide and treating with the calculated amount of bromine (2 atoms), it is converted quantitatively into dibenzoyl-dioxy-terephthalic ether (melting point 174°) with evolution of hydrobromic acid.

The above-mentioned long flat needles, having the ends cut off obliquely, remain unchanged by repeated recrystallisation, and melt sharply at 102½°. The analysis and behavior prove that these constitute a third isomer, namely, γ-dihydro-dibenzoyl-dioxy-terephthalic ether.

0.1353 gram substance, dried at 110°, gave 0.3313 gram CO_2 and 0.0642 gram H_2O.

	Theory for $H_2C_6\left\{\begin{matrix}(OCOC_6H_5)_2\\ H_2\\ (CO_2C_2H_5)_2.\end{matrix}\right.$	Found.
C	67.24	66.78
H	5.17	5.27

The substance is volatile without change; reducing agents do not reduce it further. In its behavior towards sulphuric acid and bromine it is entirely analogous to the β-isomer (*q. v.*). It is soluble with ease in all organic solvents except petroleum ether.

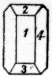
Dr. Muthmann reports the following optical properties: "Large transparent crystals. The angle of extinction found to be 14°–18°. No axis or bisectrix is seen through the predominant plane. The angle which the end planes make with the elongation of the crystal was found to vary in different specimens."

Reduction of Dibenzoyl-dioxy-terephthalic Ether with Alcoholic Hydrochloric Acid and Zinc Dust.

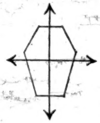
Remarkably enough, the reduction of dibenzoyl-dioxy-terephthalic ether goes in an entirely different way by using an alcoholic instead of aqueous solution of hydrochloric acid. For the reduction, alcohol saturated at 15° with hydrochloric acid was used; otherwise the method is the same as that followed above with aqueous hydrochloric acid. Fifteen minutes' reduction is sufficient, as a much longer treatment does not cause the slightest change in the composition of the reduction products, and only lowers the yield. After pouring into an excess of water, extracting with chloroform, washing with caustic alkalies, etc., there is left about 2.5 grams of reduction-product (from 5 grams substance taken). This consists of a mixture of three, probably four, isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers. One of these isomers can readily be separated from the others by fractional crystallisation from alcohol or ether. The first difficultly soluble fractions yield finally, by repeated recrystallisation, a substance crystallising in needles and melting at 165°. It is identical in every respect with the above-described α-dihydro-dibenzoyl-dioxy-terephthalic ether, and is formed here in much greater amount than by the reduction with aqueous hydrochloric acid. The isomers, more readily soluble in alcohol and ether, were repeatedly fractionated from ether with addition of a little petroleum ether. Although often large transparent measurable crystals were obtained which could be separated mechanically, and these again subjected to fractional crystallisation, it was found impossible to accomplish a sharp separation of the isomers, or to obtain single crystals which gave a sharp melting point. It was possible, however, to settle with certainty that two isomers were at hand which show a great tendency to form isomorphous mixtures, as well with one another as with α-dihydro-dibenzoyl-dioxy-terephthalic ether, wherefore it is not likely that a separation can ever be accomplished. In this way crystals were obtained melting from 85°–95°, and crystallising in long transparent rectangular plates. These often have the ends cut off obliquely in a very peculiar way and are not regularly developed. Then also crystals were observed melting between 100°–110°, and forming acute rhombic plates. The fractions most soluble in ether and petroleum ether melt at 75°–78°, and consist probably of a third isomer; but since it always separates out as an oil at first, no definite-shaped crystals can be obtained.

An optical investigation of the above crystals by Dr. W. Muthmann has proved with certainty that two distinct isomers are at hand, and that these are totally different from the above-described α, β, and γ-isomers. He reports thereon as follows:

1. "Transparent crystals, melting point 85°–95°; the above *rectangular plates*. The axial plane is perpendicular to the elongation of the crystal. Through plane 1 an optical axis comes out almost perpendicularly, the bisectrix is yet visible at the edge of the field of vision; system probably monoclinic, planes 2 and 3 prismatic, 1 and 4 ortho."



2. "The above *rhombic plates*, melting point 100°—110°. Very complete extinction noticeable, great resemblance to diacetyl-succino-succinic ether."



Although a separation of the isomers was not possible, still the above proves with certainty that at least three, and perhaps four, isomers are formed by reduction with alcoholic hydrochloric acid. That they are all dihydro-dibenzoyl-dioxy-terephthalic ethers is proved by the fact that on saponification with concentrated sulphuric acid, pure benzoic acid (melting point 120°) and pure succino-succinic ether is formed from all.

The above experiments prove conclusively that the ethers of succino-succinic ether and of dioxy-terephthalic ether have the substituted group bound to oxygen, and furthermore the behavior of the isomeric dihydro-dibenzoyl-dioxy-terephthalic ethers makes it exceedingly probable that succino-succinic ether itself is nothing but a dihydro-dioxy-terephthalic ether. That this substance ever appears as a ketone, or that it is necessary in order to explain its reactions to assume a pseudo-ketone formula, is in the present state of our knowledge of this compound without the slightest experimental proof.

Finally, there is appended a brief description of a series of compounds which completes the work on durene.[1]

Methyl dinitro-pyromellithate, made from the silver salt with methyl iodide. Transparent long flat needles, melting at 180.6° (from methyl alcohol). Analysis:

	Found.	Theory.
C	41.90 per cent.	42. per cent.
N	7.36	7.
H	3.33	3.

Methyl diamido-pyromellithate, obtained by reduction of the nitro derivative with zinc dust and acetic acid. Long flat needles (from methyl alcohol), melting at 149.6°, and possessing the color of potassium bichromate. Oxidising agents convert it not into the diimide,[2] but into a stable red azo-derivative very difficultly soluble in all solvents except hot acetic acid. Analysis:

	Found.	Theory.
C	49.40 per cent.	49.41 per cent.
H	4.94	4.71

Methyl p-diketo-hexamethylene-tetracarboxylate, or as it must now be called *methyl dihydro-dioxy-pyromellithate*, obtained by reduction of the amido compound with zinc dust and sulphuric acid. Colorless, strongly refractive cubes (from benzene) possessing a high specific gravity and a melting point 175°. The solutions show a faint blue fluorescence and give with ferric chloride a deep red coloration. Soluble in caustic, not in mild alkalies. Analysis:

	Found.	Theory.
C	48.82 per cent.	48.84 per cent.
H	4.92	4.65

Methyl dioxy-pyromellithate, obtained from the diketo compound with bromine. Granular yellow powder (from methyl alcohol) showing a green fluorescence and melting at 207°. Volatile without decomposition, but does not form good crystals. Analysis:

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[1] Annalen der Chemie **237**, 1.

[2] This Journal **11**, 5.

	Found.	Theory.
C	48.72 per cent.	49.12 per cent.
H	4.39	4.09

Methyl quinone-pyromellithate, obtained from the hydroquinone or from methyl diamido-pyromellithate by oxidation with nitric acid. Crystallises from methyl alcohol in *colorless needles*, which contain two molecules methyl alcohol.

	Theory for $C_6\left\{\begin{matrix}(CO_2CH_3)_4\\O_2\end{matrix}\right. + 2CH_4O.$	Found.
C	47.52	47.37
H	4.95	5.32

Heated to 150° it loses the crystal alcohol and changes to a pure yellow color. It then sublimes in yellow needles and melts at 208°. Analysis:

	Found.	Theory.
C	49.19 per cent.	49.41 per cent.
H	3.90	3.53

In these experiments, which were in part carried out in the chemical laboratory of Purdue University, La Fayette, Indiana, I have been most zealously assisted by Dr. V. Paepcke. It is a pleasure to me to have this opportunity of expressing to him my warmest thanks.

WORCESTER, MASS., *May* 2, 1890.

ON THE EFFECT OF TEMPERATURE UPON THE DETERMINATION OF AMMONIA BY NESSLERISATION.

BY ALLEN HAZEN AND HARRY W. CLARK.

In making a number of distillations of standard ammonium chloride solution to determine the loss due to incomplete condensation, as stated by Dr. Smart,[1] results were obtained similar to those given by him, namely, that only from 85 to 95 per cent. of the ammonia taken was found in the distillate. It was observed, however, that no more ammonia was obtained when the end of the condenser dipped below the surface of cold water, and also that by repeatedly redistilling a distillate from standard ammonium chloride solution, no more was lost than by a single distillation. The loss could not therefore be due to incomplete condensation.

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[1] Report of the National Board of Health, 1882; also this Journal **11**, 367.

The cause of this apparent loss was found to be the low temperature of the distillates. The city water, at a temperature of 5°, running about the block-tin condensers, cooled the distillate to nearly the same temperature, and the time that the tubes stood before nesslerising was insufficient to warm them to the temperature of the room. It was found that the color obtained by nesslerising an ammonia solution depends upon its temperature. The warmer the solution the deeper will be the color produced, so that a standard containing 4 cc. of ammonia solution nesslerised at 30° will give a color equal to that obtained from 5 cc. nesslerised at 15°, or 6 cc. nesslerised at 0°. A change in temperature after nesslerising will not change the color very much.

To obtain accurate results it is necessary to bring standards and distillates to the same temperature before nesslerising. This is easily accomplished by allowing them to stand in a room with even temperature for a sufficient time. It was found that the difference between the temperatures of two 50 cc. nessler tubes of water, standing side by side, was reduced to one-half every thirteen minutes. With racks of three dozen tubes each, the adjustment was much slower, forty-five minutes being required to reduce a difference of 10° to 5°. When the possible difference in temperature between different tubes at the start is 10° or more, three or four hours will be required to bring them to a sufficiently even temperature. We find it most convenient to let them stand over night. Standards and distillates are made ready for nesslerisation during the day, and all stand on the same table over night. In the morning they are nesslerised and compared. There is not the slightest loss by evaporation of ammonia in this way, even upon standing some days, and in a laboratory where ammonia fumes are excluded there is no danger of absorption of ammonia from the air.

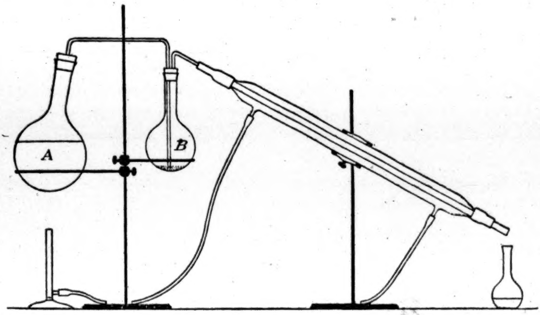
Our earlier conclusion, that there is no loss of ammonia by incomplete condensation, has been confirmed by numerous determinations made in this way, with most satisfactory results. The condenser tubes used are of block tin, twenty inches long and three-eighths inch internal diameter.

LAWRENCE EXPERIMENT STATION, MASS. STATE BOARD OF HEALTH.

APPARATUS FOR THE DETERMINATION OF AMMONIAS IN SAND AND SEWAGE.

By Allen Hazen.

In examining sand from filters it has been thought desirable to determine free and albuminoid ammonia, as this shows the amount of organic matter stored, in the same terms as it is given for the filtered water or sewage.



To accomplish this, the apparatus shown by the figure has been used during the last two years. A liter flask, *A*, filled with ammonia-free water, serves simply to supply steam. A small glass tube carries the steam to the bottom of the small flask *B*, which contains the sand. The steam passing through the sand very rapidly removes all free ammonia. Alkaline permanganate solution is then put in *B* and the distillation continued. The albuminoid ammonia is given off much more rapidly than in the ordinary water distillation, owing to the concentration of the permanganate which is put upon the sand full strength, while in water-analysis it is diluted to eight or ten times its volume by the water. One portion of 50 cc. invariably contains all the free ammonia. The first portion of albuminoid ammonia, when boiling rapidly, usually contains at least eight or nine tenths of the whole, and the second portion has almost all of the rest, so that only two tubes need be collected. Bumping is impossible. The condensation of steam in the small flask is not excessive, but if necessary it may be heated with a low flame.

I have found this apparatus to be well adapted to the examination of sewage and anything which contains enough ammonia. The great bulk of a pure water which it would be necessary to use prevents its application to ordinary water-analysis.

The amount of free ammonia thus obtained is the same as that found by the usual process of dilution with pure water and direct distillation. The albuminoid ammonia is commonly a little greater, owing to the concentration of the permanganate, but the results are sharper and different determinations agree with each other more closely. There is also a very considerable saving of time when a number of determinations are to be made.

I prefer to use rubber stoppers and connections. It requires considerable boiling to get new rubber entirely free from ammonia, but once free there is no more trouble, and a stopper will last for a very long time.

LAWRENCE EXPERIMENT STATION, MASS. STATE BOARD OF HEALTH.

ELECTROLYTIC SEPARATIONS.

BY EDGAR F. SMITH AND LEE K. FRANKEL.

In this, our third communication[1] upon the above subject, we have the following to offer. By reference to an article entitled "The Electrolytic Method applied to Palladium,"[2] it will be noticed that it was there stated that the deposition of this metal from the solution of its double cyanide was not possible so long as any undecomposed potassium cyanide remained in the solution. Acting upon this observation, we have attempted the separation of the palladium from the metals which are deposited from their double cyanide solutions, with what success the results appended will show.

Mercury from Palladium.

Solutions of mercuric chloride and of palladium chloride were used in these experiments, potassium cyanide being added, so that the precipitate first formed is completely dissolved. In the results recorded below the potassium cyanide is, as a rule, in large excess, so that there is no danger of the current precipitating any cyanides from the solution.

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[1] This Journal **12**, 104; and Proceedings of Chem. Section of Frank. Inst., Vol. I, p. 119.

[2] This Journal **12**, 212.

	Mercury present, in grams.	Palladium present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas *per* minute.	Mercury found.	Difference in percentage from theoretical.
(1)	0.0886	100 %	3	200 cc.	.08 cc.	.0891	+0.56 %
(2)	"	"	"	"	"	0.0886	...
(3)	"	"	"	"	0.1	0.0886	...
(4)	.2215	"	"	"	0.22	0.2220	+0.22
(5)	"	"	"	"	"	0.2205	—0.45
(6)	"	"	"	"	"	0.2234	+0.85
(7)	"	"	"	"	"	0.2231	+0.72
(8)	.2266	"	"	"	0.20	0.2267	+0.04
(9)	"	"	"	"	"	0.2266	...
(10)	"	"	"	"	"	0.2251	—0.66
(11)	"	"	"	"	"	0.2260	—0.26

The above figures indicate that the separation is satisfactory. In all of the experiments the current was allowed to act for sixteen hours.

Silver and cadmium being metals which, like mercury, separate quite easily and readily from cyanide solutions when acted upon by a feeble current, we naturally expected that their separation from palladium would be unattended by any particular difficulty. In this we were sadly disappointed, for out of a series of ten experiments made with varying quantities of alkaline cyanide, and with currents varying in strength from 0.5 cc. to 0.1 cc. oxyhydrogen gas per minute, we failed to obtain either silver or cadmium free from the palladium. The presence of these two metals, in fact, appeared to favor the deposition of the palladium from the solution.[1]

Mercury from Arsenic.

Our investigations with arsenic showed us that the metal could not be deposited from solutions of the alkaline arsenites or arseniates, nor from solutions containing alkaline cyanides. In the separation of mercury from arsenic, the precipitate formed on adding a solution of mercuric chloride to a solution either of potassium arsenite or arseniate was dissolved in potassium cyanide and subjected to the action of the current. The separation proceeds without any difficulty.

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[1] This Journal **12**, 213.

	Mercury present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percentage from theoretical.
(12)	0.2266	100 %	3	200 cc.	0.3 cc.	0.2277	+0.48 %
(13)	“	“	“	“	“	0.2251	—0.66
(14)	“	“	“	“	“	0.2266	...
(15)	“	“	“	“	“	0.2259	—0.30
(16)	“	“	“	“	“	0.2274	+0.35

Time of deposition was sixteen hours.

Cadmium from Arsenic.

In this instance we discovered that the separation was not complete unless the arsenic existed in the solution as the higher oxide. Experiments conducted with arsenious compounds gave a deposit of cadmium which was invariably dotted over its surface with black spots of metallic arsenic. With the arsenic present as arseniate of potassium, and with the solution for electrolysis prepared as under the separation of mercury from arsenic, the appended results were obtained.

	Cadmium present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas.	Cadmium found.	Difference in percentage from theoretical.
(17)	0.2124	100%	3	200 cc.	0.1 cc.	0.2110	—0.65%
(18)	“	“	2.2	“	“	0.2104	—0.93
(19)	“	“	“	“	0.35	0.2128	+0.19
(20)	“	“	“	“	“	0.2113	—0.52
21)	“	“	1.5	“	0.4	0.2123	—0.05
(22)	“	“	“	“	“	0.2120	—0.19
(23)	“	“	“	“	0.8	0.2123	—0.05
(24)	“	“	“	“	0.6	0.2118	—0.28
(25)	“	“	“	“	0.8	0.2120	—0.19
(26)	“	“	“	“	0.6	0.2116	—0.37

Silver from Arsenic.

The conditions essential for thorough deposition are the same here as those mentioned under the separation of cadmium from arsenic. Attempts to separate the two metals from solutions in which the arsenic existed as lower oxide resulted in the deposition of the arsenic with the silver. Using arseniate solutions, however, the results are satisfactory, as shown below.

	Silver present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Silver found.	Difference in percentage from theoretical.
(27)	0.1572	100%	2.2	200 cc.	0.15 cc.	0.1577	+0.31%
(28)	“	“	1.5	“	“	0.1572	...
(29)	“	“	2.2	“	0.3	0.1572	...
(30)	“	“	“	“	“	0.1577	+0.31
(31)	“	“	1.5	“	0.35	0.1579	+0.44
(32)	“	“	“	“	“	0.1567	—0.31
(33)	“	“	“	“	“	0.1582	+0.63
(34)	“	“	“	“	“	0.1573	+0.06

The time required for the precipitation of the metal was the same as that required for those which precede this and for those which follow, viz. sixteen hours.

Copper from Arsenic.

All that has been said concerning the separation of silver from arsenic will apply equally as well here, the only point of difference being the increased strength of current necessary for the deposition of the copper. Thrown out from such a solution, the copper appears as a firm, compact and lustrous coating; it can be readily washed and shows no tendency to oxidise. The results obtained are as follows:

	Copper present, in grams.	Arsenic present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Copper found.	Difference in percentage from theoretical.
(35)	0.1772	100%	3	200 cc.	1.5 cc.	0.1765	—0.39%
(36)	“	“	...	“	5	0.1778	+0.33
(37)	“	“	...	“	10	0.1766	—0.33
(38)	“	“	...	“	5	0.1762	—0.56

The potassium cyanide should be carefully added until the precipitate formed dissolves and the solution assumes a pink tinge. An excess of potassium cyanide is not harmful, but the greater the excess the longer will be the time required for the deposition, since the current will not deposit the copper until this excess is decomposed.

We have also attempted the separation of copper from arsenic in a solution containing an excess of ammonia.[1] The results obtained were satisfactory, but the method is one requiring skill for its successful performance and close attention to details in order to insure accurate results. From such a solution the copper is deposited as a spongy coating, and, like all such coatings, has a tendency to carry down and retain the salts of the alkalies which are in the solution. Our results are as follows:

	Copper present, in grams.	Arsenic present.	NH_4OH.	Total dilution.	Current strength in cc. OH gas per minute.	Copper found.
(39)	0.1772	100%	Large excess.	200 cc.	1.3 cc.	0.1797
(40)	“	“	“	“	0.7	0.1754
(41)	“	“	3 cc.	“	1.1	0.1783

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[1] See McCay, Chemiker Zeitung **14**, 509.

While experimenting with the oxides of tungsten and molybdenum we found that they dissolved readily in potassium cyanide, and that in such solutions, or in solutions of ammonium tungstate and ammonium molybdate in the presence of potassium cyanide, no deposition of either metal occurred, even under the influence of strong currents. With this knowledge the following separations were effected.

Mercury from Tungsten.

For this separation, weighed quantities of mercuric chloride and ammonium tungstate were dissolved in water, the precipitate of tungstate of mercury dissolved in potassium cyanide, and the resulting solution subjected to the action of the current.

	Mercury present, in grams.	Tungsten present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percentage from theoretical.
(42)	0.2266	100%	2.2	200 cc.	0.7 cc.	0.2282	+0.70%
(43)	"	"	3	"	0.8	0.2282	+0.70
(44)	"	"	2.2	"	"	0.2268	+0.09
(45)	"	"	1.5	"	0.7	0.2281	+0.66
(46)	"	"	1.5	"	"	0.2280	+0.61

By employing solutions of ammonium tungstate, mercuric chloride and potassium cyanide, in the amounts indicated above, the deposition of the mercury will follow without carrying down with it any tungsten as oxide. It was noticed that when the current strength exceeded that given in the experiments, a slight coating of oxide of tungsten made its appearance on the mercury, although it seemed to be fully removed during the process of washing. The slightly higher results found in the table are not, however, due to this cause. Tungsten was not found in these deposits, though careful search was made for it.

Silver from Tungsten.

The conditions essential for this separation are the same as those in the preceding.

	Silver present, in grams.	Tungsten present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Silver found.	Difference in percentage from theoretical.
(47)	0.1572	100 %	1.5	200 cc.	0.7 cc.	0.1566	—0.38 %
(48)	"	"	"	"	"	0.1580	+0.50
(49)	"	"	1	"	"	0.1579	+0.44
(50)	"	"	"	"	"	0.1587	+0.95
(51)	"	"	"	"	"	0.1579	+0.44
(52)	"	"	.75	"	"	0.1583	+0.70

Cadmium from Tungsten.

In this separation, the condition of extreme importance is the strength of current. It was found that if the current used was stronger than that mentioned in the following table, the deposits were apt to become spongy and the results correspondingly high.

	Cadmium present, in grams.	Tungsten present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Cadmium found.	Difference in percentage from theoretical.
(53)	0.2408	100 %	2.2	200 cc.	0.6 cc.	0.2422	+0.58 %
(54)	"	"	1.5	"	"	0.2396	—0.49
(55)	"	"	"	"	"	0.2408	...
(56)	"	"	"	"	"	0.2425	+0.70
(57)	"	"	"	"	"	0.2411	+0.12
(58)	"	"	"	"	"	0.2409	+0.04

Mercury from Molybdenum.

The method utilised here was the same as the one found effective in the separation from tungsten. The precipitate obtained on adding mercuric chloride to the solution of ammonium molybdate was dissolved in potassium cyanide and then exposed to the action of the current. The results found and the conditions necessary are indicated in the table.

	Mercury present, in grams.	Molybdenum present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Mercury found.	Difference in percentage from theoretical.
(59)	0.2266	100 %	1.5	200 cc.	1 cc.	0.2271	+0.22 %
(60)	"	"	2.2	"	"	0.2283	+0.79
(61)	"	"	3	"	"	0.2273	+0.30
(62)	"	"	2.2	"	"	0.2272	+0.26
(63)	"	"	3	"	"	0.2275	+0.35

Silver from Molybdenum.

The silver was added in the form of nitrate, the conditions otherwise being similar to those under the separation of mercury from molybdenum.

	Silver present, in grams.	Molybdenum present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Silver found.	Difference in percentage from theoretical.
(64)	0.1572	100 %	1.5	200 cc.	0.8 cc.	0.1576	+0.25 %
(65)	"	"	2.2	"	0.8	0.1580	+0.50
(66)	"	"	3	"	0.4	0.1583	+0.70
(67)	"	"	1.5	"	"	0.1573	+0.06
(68)	"	"	2.2	"	"	0.1578	+0.38

Cadmium from Molybdenum.

In these separations, the tendency of the cadmium to form spongy deposits was not so noticeable. In most cases the coating was dense and compact, and hence permitted thorough washing.

	Cadmium present, in grams.	Molybdenum present.	KCN in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Cadmium found.	Difference in percentage from theoretical.
(69)	0.2408	100 %	2.2	200 cc.	0.4 cc.	0.2392	—0.66 %
(70)	"	"	1.5	"	"	0.2431	+0.91
(71)	"	"	"	"	"	0.2416	+0.33
(72)	"	"	2.2	"	"	0.2410	+0.08
(73)	"	"	3	"	"	0.2400	—0.33

Copper from Bismuth.

So far as we are aware, there has not as yet been a successful method proposed for the electrolytic separation of these two metals. Knowing that bismuth[1] could be completely deposited from solutions of the citrate containing excess of alkali, we added to such a solution copper sulphate and then a slight excess of potassium cyanide, and found that under such conditions the bismuth was deposited without carrying down with it any of the copper. Having convinced ourselves that this was true, we instituted the following separations, which prove the accuracy of the method. It is necessary for complete deposition that sufficient citrate and alkali be present to keep the solution clear upon the addition of the potassium cyanide.

	Bismuth present, in grams.	Copper present.	Citric acid present, in grams.	Total dilution.	Current strength in cc. OH gas per minute.	Bismuth found.	Difference in percentage from theoretical.
(74)	0.0946	...	3	200 cc.	1 cc.	.0952	+0.63 %
(75)	"	...	"	"	"	.0940	—0.63
(76)	"	...	"	"	"	.0948	+0.21
(77)	"	100 %	"	"	"	.0949	+0.31
(78)	"	"	"	"	"	.0941	—0.51
(79)	"	"	"	"	"	.0947	+0.10
(80)	"	"	"	"	"	.0947	+0.10
(81)	"	"	"	"	"	.0947	+0.10

While these figures indicate a complete separation, we would advise careful compliance with the conditions of the experiment, otherwise the results will prove to be discordant. The deposit often occurs spongy and is apt to loosen from the dish on washing, so that great care is necessary at this point.

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[1] This Journal **5**, 114.

In all of the separations mentioned above we washed the deposited metal with boiling water, except in the case of bismuth, where washing with cold water and absolute alcohol proved decidedly advantageous. The drying was done upon a moderately warm iron plate. The current used in all cases was derived from Daniell cells of the crowfoot pattern.

UNIVERSITY of PENNSYLVANIA, *April* 30, 1890.

Contributions from the Laboratory of Purdue University.

III.—UPON THE CARBOHYDRATES OF PEACH GUM.

BY W. E. STONE.

A certain class of vegetable products known as "gums" or "mucous" or mucilage yield as the result of hydrolytic action, glucose-like bodies. These, whenever carefully studied, have, almost without exception, been identified as either *galactose* or *arabinose.* When heated with a dilute solution of sulphuric acid, gum arabic yields sometimes galactose and sometimes arabinose,[1] although it is not quite clear whether this is a specific characteristic of a distinct gum, or whether there may not be gums of different origins sold under the one name. The gum exuding from the bark of the cherry tree produces by hydrolytic action, *arabinose.*[2] Tragacanth gum yields the same product.[3] The mucilage occurring in the seed-coats of linseed, quince seeds, etc., yields also glucoses, which, however, have not been satisfactorily isolated or identified. A gum-like substance which can be extracted from lignified tissues by alkalies yields by hydrolysis, *xylose.*[4] A gum exudes from the bark of the peach tree (*Persica vulgaris*) following injury, or from the fruit of the same when punctured by insects, which, with one exception, has not been studied. The wild peach tree, escaped from cultivation in the middle southern United States, produces this gum in considerable quantities, and from this source I obtained 200–300 grams, in air-dried weight, of gum as collected from the bark, and a somewhat less quantity from the fruit. The former was of a dark brown color and contained many impurities, such as bits of bark, leaves, etc.; that from the fruit exuded in clear drops, which soon hardened on exposure to the air to transparent or semi-opaque tears, and was of course of a higher grade of purity than that from the bark.

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[1] Claesson, Ber. d. chem. Gesell. **14**, 1270.

[2] Claesson, Sachsse u. Martin, Phytochemische Untersuchung, 69.

[3] Sandersleben, Ibid.

[4] Koch, Pharmaceutische Zeitschrift für Russland **25**. Also Wheeler and Tollens, Ber. d. chem. Gesell. **22**, 1046.

This gum was soluble in water, by which it first became swollen to a marked degree, and in solution showed a slightly acid reaction, and a distinct, although not strong, laevo-rotation.

After my investigation had been in progress some time I learned of R. W. Bauer's results obtained from peach gum which was probably of European origin. By treating the same with a dilute solution of sulphuric acid he secured a crystalline sugar-like substance which possessed the specific rotation $(\alpha)_D = 76.02°$, and which he regarded as identical with galactose, although lack of material had evidently prevented confirmatory tests. From this he concluded that the peach gum contained the carbohydrate from which galactose is derived by hydrolysis. A preliminary examination of the gum in my possession indicated, however, that it also contained the substance from which arabinose is derived, as well as that mentioned by Bauer, and this was confirmed by further investigation.

The two portions of gum were examined separately, although all stages of the examination showed them to be of practically the same nature. As preliminary to a close study, portions of both gums were subjected to the furfurol test for the presence of an arabinose-producing substance,[1] and to the mucic acid test for a similar source of galactose.[2]

By distillation at 125°–130° C. with sulphuric acid kept at a constant density of 1.254, concentration of the distillate, and precipitation with dilute ammonia, the following data were obtained:

Gum from bark:—2.5 grams yielded .1181 gram of furfuramide, or 4.72 per cent.

Gum from fruit:—2.5 grams yielded .1214 gram of furfuramide, or 4.84 per cent.

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[1] Stone and Tollens, Ann. Chem. (Liebig) **249**, 227.

[2] Kent and Tollens, Ann. Chem. (Liebig) **227**, 228.

By oxidation with nitric acid of 1.15 specific gravity, mucic acid was produced as follows:

Gum from bark:—5 grams yielded .618 gram of mucic acid, or 12.36 per cent.

Gum from fruit:—2.5 grams yielded .423 gram of mucic acid, or 16.92 per cent.

These results indicated the presence in the gum of those substances which yield *arabinose* and *galactose* upon hydrolysis, and the course of the investigation was directed toward isolating and identifying the same. 110 grams of the gum from the bark of the peach tree were dissolved in 880 cc. of dilute sulphuric acid of 1.03 specific gravity, and the solution heated on the water-bath for ten hours. At the end of this time the liquid was of a dark amber color, much humin-like substance had been separated, and the vapors gave an intense red color upon paper moistened with aniline acetate, indicating the formation of furfurol. The liquid was neutralised with barium carbonate, filtered and evaporated, yielding a thick dark-colored sirup which reduced Fehling's solution strongly. In the same way 50 grams of the gum from the peach fruit were dissolved in 400 cc. of dilute sulphuric acid of 1.03 specific gravity, and heated during nine hours with the same results as in the previous case.

The dark-colored impure sirups thus obtained were boiled with strong alcohol for about an hour, whereby a dark gummy substance was precipitated. From this the clear alcoholic solution was decanted and again evaporated, after which crystallisation soon followed. In this way 21.3 grams of a white crystalline product were obtained from the bark gum, or nearly 20 per cent. of the material taken. From the fruit gum a proportionally smaller quantity was obtained. Both products were sweet, and reduced Fehling's solution strongly. After recrystallisation, the specific rotations of each were determined as follows:

From bark gum:—3 grams in a solution of 30 cc. showed an average dextro-rotation of 19.16° or $(\alpha)_D = 98.4°$.

From fruit gum:—3 grams in a solution of 30 cc. showed an average dextro-rotation of 19.04° or $(\alpha)_D = 95.2°$.

These numbers indicated the identity of the two products, but did not correspond to the specific rotations of any of the known glucoses or sugar-like bodies, although that of the product from bark gum approximated the specific rotation of arabinose. They differed also decidedly from Bauer's result ($(\alpha)_D = 76.02°$). A mixture of two substances like arabinose and galactose, however, would give a polarising number like that obtained. Moreover, the preliminary tests for mucic acid and furfurol had indicated the formation of both of these compounds. The next step, therefore, was an attempt to separate these products by means of fractional crystallisation into their constituents. By crystallisation from absolute alcohol each of the two original products was separated into several portions, the specific rotations of which showed a curious relation to that of the original substance.

From the sugar from bark gum, which showed the specific rotation of 98.4°, five fractions were obtained, which, in the order of their separation, showed the following polarising numbers:

I. $(\alpha)_D = 97.5$
II. " $= 73.5$
III. " $= 93.0$
IV. $(\alpha)_D = 94.3$
V. " $= 96.3$

The sugar from fruit gum, which had the specific rotation 95.2, was separated into two portions, which gave the following polarising numbers:

I. $(\alpha)_D = 75.0$
II. $(\alpha)_D = 94.8$

In both cases it is to be noted that a fraction was separated with a much lower specific rotation than the original without increasing the specific rotation of the other fractions. These fractions ultimately included all of the mother-liquor; hence it may not be assumed that a higher polarising sugar remained in solution. In the sugar from fruit gum it is certainly remarkable that the original portion polarising 95.2° should have been resolved into one polarising 75.0° and another polarising at 94.8°, which latter number is practically the same as the original. There was no marked disproportion in the quantity of the fractions. The separations were made from alcohol at the ordinary laboratory temperature, which conditions could scarcely affect or change the specific rotations of the bodies in solution.

Of the fractions from the sugar from bark gum, numbers I, II and III, while not agreeing exactly with the polarisation constants for arabinose and galactose, still approached them. They were therefore recrystallised and gave respectively the following numbers:

Ia, $(\alpha)_D = 98.8°$
IIa, " $= 82.09°$
IIIa, " $= 98.9°$

In like manner also the fractions from the sugar of the fruit gum were recrystallised. I. was unfortunately lost by an accident, but its specific rotation, as already observed (75.0°), leaves little doubt that it would also have given a result similar to that of II. of the bark-gum product. II. showed after recrystallisation the specific rotation 101.6°.

Nos. Ia and IIIa of the product from the bark gum were again recrystallised and yielded a product with the specific rotation $(\alpha)_D = 102.3°$. As results, therefore, of these repeated and tedious fractional separations, there were obtained, from the bark gum, two products: one with the specific rotation 102.3°, which approximated very closely that of arabinose (104°), and a second with the specific rotation 82.09°, which is practically that of galactose. From the fruit gum also we obtained two products which were undoubtedly identical with those from the bark gum, and which according to their specific rotations were also respectively arabinose and galactose.

These comparatively pure products were now subjected to some confirmatory tests in order to leave no doubt as to their nature.

Arabinose being a pentaglucose, $C_5H_{10}O_5$, has in common with xylose, the only other known member of the class, the characteristic reaction of producing furfurol in large quantities when distilled with sulphuric acid.[1] Xylose, however, has the specific rotation $(\alpha)_D = 18°–19°$,[2] and was therefore quite out of the question in connection with the body already described with the specific rotation 102.3°. 0.9246 gram of the latter was distilled with sulphuric acid of 1.254 specific gravity (the loss by distillation being replaced by a regular constant addition of water to the distilling flask), until the distillate no longer gave a distinct coloration on paper moistened with aniline acetate. The distillate being then concentrated by fractional distillation and treated with dilute ammonia gave a precipitate of furfuramide, which on being dried weighed 0.1843 gram, or 19.93 per cent. of the weight of sugar taken. This result taken with the specific rotation leaves no doubt as to the identity of this product with arabinose. From a very small quantity a phenylhydrazine compound was prepared, which was, however, insufficient for recrystallisation, and, in the impure state, showed the melting point of 145°.

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[1] Loc. cit.

[2] Wheeler and Tollens, Ber. d. chem. Gesell. **22**, 1046.

A well known specific reaction for galactose is the formation of mucic acid when subjected to the action of nitric acid. The other portion of sugar from bark gum, polarising at 82.09°, was heated on a water-bath with nitric acid of 1.15 specific gravity. 0.5025 gram received 20 cc. of nitric acid, and the whole was heated until two-thirds of the original volume was evaporated. 0.288 gram of mucic acid was thus produced, or 57.3 per cent. of the weight of sugar taken. A phenylhydrazine compound was also formed which melted at 154°. These reactions, coupled with the specific rotation, identifies the second product as galactose.

The gummy substance secreted from the tissues of the peach tree, as above described, contains, therefore, those bodies which by hydrolysis yield arabinose and galactose. The occurrence of these bodies together under these circumstances is the more noteworthy from the fact that arabinose and galactose represent two distinct classes of carbohydrates, the true glucoses and the pentaglucoses, and are not usually found in such intimate connection with each other. The gum arabic is, I believe, the only other instance where such occurrence has been recognised, and in no previous case has the isolation and recognition of both these carbohydrates from a single homogeneous substance been accomplished.

LA FAYETTE, IND., *May*, 1890.